UNIVERSITÄT KOBLENZ · LANDAU

ENVIRONMENTAL AND SOIL CHEMISTRY

DFG

# International Workshop

## Nanoparticles in Soils and Waters: Fate, Transport and Effects

InterNano

*11th - 13th March, 2014*

Landau in der Pfalz, Germany

# Organisation and Financial Support

## Steering Committee:

Gabriele E. Schaumann
*University of Koblenz-Landau, Landau, Germany*

Thomas Baumann
*Technical University of Munich, Munich, Germany*

Reinhard Niessner
*Technical University of Munich, Munich, Germany*

Friederike Lang
*University of Freiburg, Freiburg, Germany*

Werner Manz
*University of Koblenz-Landau, Koblenz, Germany*

Ralf Schulz
*University of Koblenz-Landau, Landau, Germany*

Hans Jörg Vogel
*Helmholtz Centre for Environmental Research, Leipzig/Halle, Germany*

## Local Organizing Committee

Gabriele E. Schaumann, George Metreveli and Angelika Holderle
*University of Koblenz-Landau, Landau, Germany*

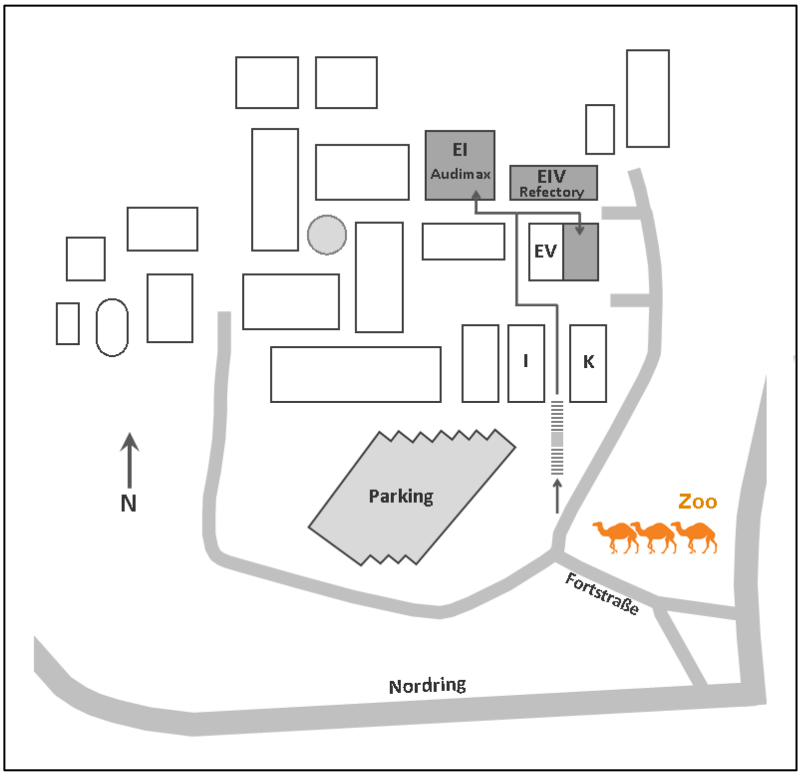
## Financial Support

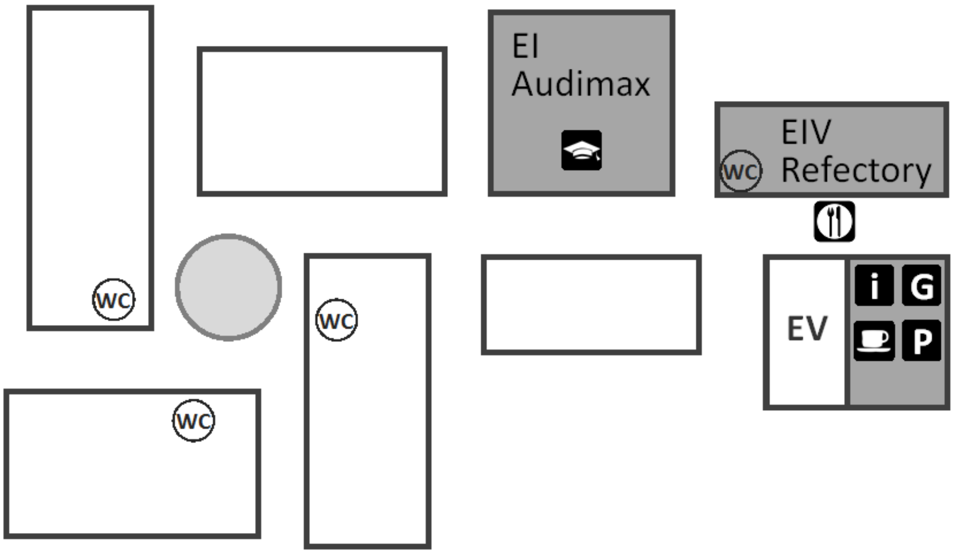
We acknowledge financial support from the German Research Foundation (Deutsche Forschungsgemeinschaft DFG) within the INTERNANO project "Mobility, aging and functioning of engineered inorganic nanoparticles at the aquatic-terrestrial interface" (FOR 1536).

# Table of Contents

# Map

UNIVERSITÄT KOBLENZ · LANDAU





| | |
|---|---|
| i | Conference registration and information desk |
| 🎓 | Oral presentations |
| P | Poster sessions |
| G | Get-together |
| ☕ | Coffee breaks |
| 🍴 | Lunch |
| WC | Toilets |

## Landau in der Pfalz

The town of Landau is located in the district of southern Rhineland-Palatinate and is characterized by the culinary delights of viniculture and the cuisine of Palatinate and nearby France. The beautiful town center with an ample pedestrian area, neat parks, a lively market and friendly people tells a turbulent history. Landau is surrounded by vineyards and villages of the scenic German Wine Route and the Palatinate Forest invites for recreation. Workshop host is the University of Koblenz-Landau with the campus on the remains of the French star fort.

The autonomous city is surrounded by the "Southern Wine Route" and is a long-standing cultural center and a market and shopping town in the heart of the Palatinate wine region. Additionally, its neighborhood to Europe's largest contiguous forest, the Palatinate forest, and its long history with beautiful main sights like the main square (Rathausplatz) and the market hall (Altes Kaufhaus) makes it always worth a visit.

## Campus Landau

The University of Koblenz-Landau is one of the youngest universities in Germany. It was transformed from a teacher's training college to a modern and research-orientated university in 1990. Since then, new Departments and Institutes have been founded and the university expanded and raised its research profile in Psychology, Education, Humanities and Natural Science.

Research at Koblenz-Landau is above all oriented towards practical application. The transfer of academic work through co-operation with partners from industry, commerce and administration is of great importance. As a young university it has the necessary openness and flexibility to respond to the demand for work in the realms of research, development, consultancy, and provision of expert opinion.

A special feature of the University of Koblenz-Landau is its structure. Koblenz and Landau are the locations for research, teaching, and further education. The organizing link between the two campuses is the President's Office in Mainz, home of the university executive and the central university administration.

## Institute for Environmental Sciences Landau

The focus of the research at the Institute for Environmental Sciences concentrates on new anthropogenic stressors in linked ecological systems. Transition zones between ecological systems contribute substantially to the regional biodiversity and are „hotspots" for many ecological and biogeochemical processes. They provide many „ecosystem services", like flood protection, retention and degradation of pollutants as well as the conservation of biodiversity and recreational areas, and are of high socio-economical importance. At the same time they are considered as particularly sensitive to environmental changes, e.g. by changing flooding dynamics as consequence of anthropogenic operations or global climate change.

Pronounced goal of the Institute for Environmental Sciences is the study of these interactions in interdisciplinary co-operation between the biologically, chemically, physically, geo-scientifically and sociologically aligned working groups

| Tuesday, March 11, 2014 | |
|---|---|
| 18:00 | Get-together Party, Room: Refectory |

| Wednesday, March 12, 2014 | | |
|---|---|---|
| 8:00 | **Registration opens** | |
| 8:30 | Welcome, Room: Audimax | |
| **Session: Fate and Transport**<br>Room: Audimax | | |
| 8:45 | **Keynote** *G. V. Lowry* | Measuring and modeling behaviors of nanoparticles in realistic complex environments |
| 9:15 | *N. Sani-Kast, A. Praetorius, M. Scheringer, J. Labille, P. Ollivier, and K. Hungerbühler* | The effect of complex environmental conditions on the fate of engineered nanoparticles (ENP) in surface water |
| 9:35 | *C. Nickel, B. Hellack, A. Nogowski, F. Babick, M. Stintz, and T. A. J. Kuhlbusch* | Environmental media induced changes of surface functionalisation of two titanium dioxide nanomaterials |
| 9:55 | *I. Toloni, F. Lehmann, and P. Ackerer* | Water velocity effects on $TiO_2$ nanoparticle transport in porous media: measurements and modeling |
| 10:15 | Coffee Break<br>Room: Refectory | |
| 10:40 | *S. Klitzke, G. Metreveli, and F. Lang* | Fate of synthetic Ag nanoparticles in soils – aggregation and surface coverage through sorption of solutes |
| 11:00 | *J. Filip, F. Karlický, Z. Marušák, J. Kašlík, J. Nosek, M. Stavělová, M. Otyepka, and R. Zbořil* | Mechanism and kinetics of iron nanoparticles oxidation in water: laboratory versus field study |
| 11:20 | *A. Matheis, N. Klaas, and J. Braun* | Reactivity, longevity and characteristic of nano zero valent iron particles for groundwater remediation |
| 11:40 | *I. Sabbah, Y. Haimov, and N. Mor* | Fate of natural and naturally modified engineered nano-particles related to in-situ remediation of soil and groundwater contamination |
| 12:00 | Lunch<br>Room: Refectory | |
| 14:00 | **Keynote** *R. Kaegi, B. Thalmann, A. Voegelin, and E. Morgenroth* | Transformations silver nanoparticles in urban wastewater systems |
| 14:30 | *M. Burkhardt, S. Stähli, B. Sinnet, and R. Kägi* | Diffuse discharge of $TiO_2$ from landfills to the environment |
| 14:50 | *K. Miyajima and J. Braun* | In-situ groundwater remediation using nanoparticles: large scale experiments for investigation of transport and reactivity |
| 15:10 | *C. Neukum* | Mobility of stabilized silver nanoparticles in fissured sandstone |
| 15:30 | Coffee Break<br>Room: Refectory | |
| 15:55 | *Y. Liang, S. A. Bradford, J. Simunek, M. Heggen, H. Vereecken, and E. Klumpp* | Retention and remobilization of stabilized silver nanoparticles in soils |
| 16:15 | *I. Dror and B. Berkowitz* | The transport and impact of metal nanoparticles in soil |
| 16:35 | *A. Braun, C. Neukum, and R. Azzam* | Transport and retention of engineered silver nanoparticles in natural soils |
| 16:55 | *S. K. Kumahor and H.-J. Vogel* | A new approach to studying fate and transport of nanoparticles under unsaturated conditions |
| 17:30 - 19:00 | **Posters & Wine**<br>Room: Refectory | |

|  |  |  |
|---|---|---|
| **Thursday, March 13, 2014** |  |  |
| **Session: Toxicity**<br>Room: Audimax |  |  |
| 8:30 | **Keynote** A. A. Koelmans | Nanoparticles in the aquatic environment |
| 9:00 | *A. J. Wyrwoll, P. Lautenschläger, A. Bach, A.Schäffer, and H. M. Maes* | Looking beyond standard testing of $TiO_2$ nanomaterials – consideration of solar radiation in the *Daphnia* sp. acute immobilization test |
| 9:20 | *F. Seitz, R. R. Rosenfeldt, S. Schneider, R. Schulz, and M. Bundschuh* | Particle characteristic related effects of titanium dioxide nanoparticles on *Daphnia magna* and *Gammarus* |
| 9:40 | *R. R. Rosenfeldt, F. Seitz, J. Höger, A.-C. Haigis, R. Schulz, and M. Bundschuh* | Factors triggering the combined toxicity of nanosized titanium dioxide and heavy metals |
| 10:00 | Coffee Break<br>Room: Refectory |  |
| 10:25 | *M. Weil, T. Meißner, A. Springer, W. Busch, D. Kühnel, and K. Duis* | The nanocomposite Carbo-Iron® shows no adverse effects on growth, survival and gene expression in |
| 10:45 | *E. J. Joner* | Hazards of zero-valent iron nanoparticles used for soil and groundwater remediation |
| 11:05 | *A. Grün, C. App, A. Breidenbach, J. Meier, and W. Manz* | Impact of silver nanoparticles on bacterial biofilms – *monospecies* vs. natural biofilms |
| 11:25 | *D. W. Britt, C. O. Dimkpa, J. E. McLean, N. Martineau, R. Haverkamp, and A. J. Anderson* | Silver nanoparticle uptake and growth inhibition in wheat |
| 11:45 | Lunch<br>Room: Refectory |  |
| 13:45 | *C. Emmerling and M. Hänsch* | Evaluation of the eco-toxicological relevance of silver nanoparticles in soil |
| 14:05 | *G. Metreveli, F. Seitz, A. Grün, M. Bundschuh, R. Schulz, W. Manz, and G. E. Schaumann* | Dispersion and stability of silver nanoparticles in different ecotoxicological test media |
| 14:25 | *T. Meißner, K. Oelschlägel, and A. Potthoff* | Sonication of nanomaterials used in toxicological studies |
| 14:45 | Coffee Break<br>Room: Refectory |  |
| **Session: Analytics**<br>Room: Audimax |  |  |
| 15:10 | **Keynote** M. Borkovec | Tuning Stability of Nanoparticle Suspensions by Polyelectrolytes |
| 15:40 | *A.-L. Fabricius, L. Duester, B. Meermann, and T. Ternes* | ICP-MS-based characterization of inorganic nanoparticles – sample preparation and off-line |
| 16:00 | *M. Kühn, N. P. Ivleva, R. Niessner, and T. Baumann* | Stability and effects of natural coatings on engineered inorganic nanoparticles (EINP) investigated by surface enhanced raman spectroscopy (SERS) |
| 16:20 | *A. Philippe, D. Rakcheev, and G. E. Schaumann* | Evaluation of hydrodynamic chromatography coupled with ICP-MS for the detection and quantification of inorganic colloids in environmental matrixes |
| 16:40 | *A. Fritzsche, J. Bosch, T. Ritschel, M. Händel, R. U. Meckenstock, and K. U. Totsche* | FTIR spectroscopy-based assessment of mobile goethite colloids after injection into a BTEX-contaminated aquifer - a field study |
| 17:00 | *N. Gottselig, R. Bol, V. Nischwitz, H. Vereecken, and E. Klumpp* | Fine colloidal and nanoparticulate P, Fe, Al and C distribution in stream water of a German mountainous forest catchment |
| 17:30 - 19:00 | **Posters & Wine**<br>Room: Refectory |  |

**Gregory V. Lowry**

*Carnegie Mellon University, Pittsburgh, United States*

**Michal Borkovec**

*University of Geneva, Geneva, Switzerland*

**Ralf Kaegi**

*Eawag, Dübendorf, Switzerland*

**A.A. (Bart) Koelmans**

*Wageningen University, Wageningen, Netherlands*

# Oral Session

# Fate and Transport

*Wednesday, March 12, 2014*
Room: Audimax

*Keynote*

## Measuring and modeling behaviors of nanoparticles in realistic complex environments

*Gregory V. Lowry*
Carnegie Mellon University, Civil & Environmental Engineering, Pittsburgh, Center for Environmental Implications of Nanotechnology (CEINT)

E-mail: glowry@cmu.edu

### Abstract

Engineered nanomaterials are kinetically metastable materials and are typically highly reactive. They and therefore are expected to be transformed by components in the environment. Many nanomaterials are also made from ecotoxic metals or can produce reactive oxygen that may be harmful to organisms. As such, it is logical to expect that the environment will change the ENM, and that the ENM will change to environment. In complex natural media, complicated feedback loops between the ENMs and the environment can occur and lead to different ecological responses even for very similar nanomaterials. Mesocosm and laboratory studies containing a sufficient degree of complexity are needed to provide information on how engineered nanomaterials will behave in real environments, and will (or will not) lead to unwanted impacts. This lecture will present some of the complicated feedbacks loops observed in large scale freshwater ecosystems including aggregation, dissolution, sulfidation, plant uptake and toxicity, and interaction with organic matter that together affect the ecological endpoints of the study. These large studies are complimented with better controlled laboratory studies and with models developed to identify the interplay between environmental conditions and the behaviors and effects of engineered nanomaterials on selected organisms.

# The effect of complex environmental conditions on the fate of engineered nanoparticles (ENP) in surface water

*Nicole Sani-Kast*[1], *Antonia Praetorius*[1], *Martin Scheringer*[1], *Jerome Labille*[2], *Patrick Ollivier*[3], *and Konrad Hungerbühler*[1]

[1] ETH Zurich, Zürich / Switzerland

[2]CEREGE UMR 6635 CNRS/Aix-Marseille Université, Europôle de l'Arbois, Aix-en-Provence / France

[3]Bureau de recherches géologiques et minières (BRGM), UMR 7327, BP 36009, Orléans / France

E-mail: nicole.sani.kast@chem.ethz.ch

## Abstract

Risk assessment for engineered nanoparticles (ENPs) has to rely on predicted ENP emissions and environmental concentration since ENP detection in the environment is not yet feasible. Like other colloidal materials ENP form unstable systems that are strongly influenced by the surrounding conditions (e.g. pH, temperature and ionic strength). Since the incorporation of complex environmental conditions in laboratory settings is deemed almost impractical, realistic ENP concentrations in the environment are better determined by using environmental fate models. Here we present the development and assessment of such a fate model. In order to simulate realistic conditions we chose to evaluate our methodology by simulating the fate of nano-$TiO_2$ in the Lower Rhône River (France). To this end we used measured river properties obtained from a designated sampling campaign of this river. The sampling provided us with SPM composition and characterization and water chemical composition at nine strategic points along the river. The measured properties were incorporated in a box model yielding, amongst other, dynamical SPM distribution along the river. Next, different nano-$TiO_2$ emission scenarios were simulated. Since the ability of SPM to aggregate with ENP was demonstrated by several studies to profoundly influence ENP fate, we focused our attention mainly on this transport mechanism. By considering all combinations of aggregation affinities between the measured SPM species and nano-$TiO_2$ we were able to assemble a comprehensive transport profile and predict realistic nano-$TiO_2$ concentrations in the Lower Rhône River. This methodology is a novel approach that addresses the lack of measured ENP concentrations in the environment. We proved that computational fate models, incorporating measured environmental data, make it possible to substantially reduce the range of possible environmental concentration of ENP.

**Keywords:** engineered nanoparticles, fate, surface water, realistic conditions.

# Environmental media induced changes of surface functionalisation of two titanium dioxide nanomaterials

*Carmen Nickel*[1], *Bryan Hellack*[1], *André Nogowski*[2], *Frank Babick*[2], *Michael Stintz*[2], *and Thomas A.J. Kuhlbusch*[1,3]

[1]Air Quality & Sustainable Nanotechnology, Institute of Energy and Environmental Technology (IUTA) e.V., Duisburg / Germany

[2]Institute of Process Engineering and Environmental Technology, Technical University, Dresden / Germany

[3]Center for Nanointegration, University Duisburg-Essen, Duisburg / Germany

E-mail: nickel@iuta.de

## Abstract

$TiO_2$-nanomaterials are already used in several consumer products. For their application the $TiO_2$ nanoparticles are often functionalised to avoid or favour a specific behaviour.

The aim of the investigation was to determine the possible degradation or change of the origin surface functionalisation and coating of two different $TiO_2$ nanomaterials, which are used in sunscreens under varying conditions. Any change of the coating may affect the fate and behaviour of the nanomaterial in the environment which is very important for transport, bioavailability and hence risk assessment.

Both tested $TiO_2$-nanomaterials are coated with $Al_2O_3$ to avoid photocatalytic activity. A further functionalisation with dimethicone or glycerol is applied to ensure hydrophobic and hydrophilic behaviour, respectively. Possible changes of the surface coating and functionalisation were determined by the amount of the dissolved coating material in the supernatant as well as by the changes in the behaviour of the suspended nanomaterials when environmental parameters like pH, $CaCl_2$ or humic acid concentrations were varied.

The analyses of the supernatant in deionised water after three different dispersion procedures revealed that around 90% of the glycerol as well as of the dimethicone was washed off from the surface. After the materials having been suspended in deionised water, both materials showed also a similar behaviour with a point of zero charge around pH 8.5, which corresponds to that of $Al_2O_3$ rather than $TiO_2$. The latter finding was confirmed by the result that both materials did not show intrinsic hydroxyl radical generation even after intense treatment with complete/sun-like light spectrum. The variation of further parameters effected the stability of the nanomaterialsuspension. An increased ionic strength, resulted in destabilisation due to reduced double layer thickness, whereas an increased humic acid concentration leads to a stabilisation, by electrostatic and steric repulsion.

Acknowledgement: This work was sponsored by the German Environmental Agency (UBA).

**Keywords:** $TiO_2$ nanomaterials, coating stability, transformation processes, environmental behaviour

# Water velocity effects on $TiO_2$ nanoparticle transport in porous media: measurements and modeling

*Ivan Toloni, François Lehmann, and Philippe Ackerer*
Laboratoire d'Hydrologie et de Géochimie de Strasbourg, UdS-CNRS UMR 7517, Université de Strasbourg, Strasbourg / France

E-mail: ivan.toloni@etu.unistra.fr, lehmann@unistra.fr, ackerer@unistra.fr

## Abstract

Column experiments were conducted in order to investigate transport and retention of titanium dioxide (TiO2, rutile) nanoparticles in water saturated porous media. Laboratory columns were packed as uniformly as possible with quartz sand so as to get the same hydrodynamic parameters for each experiment (porosity, dispersivity). Transport experiments were carried out, at least in duplicate, under a range of ionic strength (IS) and water velocity (U). At both the top and the bottom of the column, conductivity, pH and UV-absorption (280 nm) were automatically monitored all along the experiments by means of on-line sensors.

The obtained $TiO_2$ break through curves (BTC) had a shape characterized from the time increasing concentration, typically related to blocking retention mechanism. Mass retention decreased with an augmentation of U and increased with an augmentation of the IS of the solution. A transport model coupling convective-dispersive transport with a kinetic deposition was used to fit the BTC. A Langmuirian dynamics was proposed for kinetic deposition, coherently with the blocking mechanism that controls the BTC shape. The deposition term depends on two parameters: the deposition coefficient ($k_d$ [$s^{-1}$]) and the maximum solid phase concentration (Smax, [mg/g]). The parameters were optimized for each BTC through the resolution of an inverse problem using the software HYDRUS 1D. An analysis was conducted to relate the optimized parameters with the filtration theory.

**Keywords:** nanoparticles, $TiO_2$, transport, retention, saturated porous media.

# Fate of synthetic Ag nanoparticles in soils – aggregation and surface coverage through sorption of solutes

*Sondra Klitzke*[1], *George Metreveli*[2], *and Friederike Lang*[3]

[1]Chair of Soil Ecology, University of Freiburg, Freiburg im Breisgau/Germany; Department of Soil Science, Berlin University of Technology, Berlin / Germany

[2]Deptartment of Soil and Environmental Chemistry, Institute of Environmental Sciences, University of Koblenz-Landau, Landau / Germany

[3]Chair of Soil Ecology, University of Freiburg, Freiburg im Breisgau / Germany

E-mail: sondra.klitzke@tu-berlin.de, metreveli@uni-landau.de, fritzi.lang@bodenkunde.uni-freiburg.de

## Abstract

Synthetic inorganic nanoparticles (NP) enter the soil through different pathways, where their stability is affected by various processes. Sorption to silica surfaces is reported to decrease with increasing negative particle charge. Several publications indicate an increased NP stability following DOC sorption. Therefore, we tested the following hypothesis: (A) Bare AgNP show stronger sorption to soil particles than those stabilized through additional charges. (B) The colloidal stability of NP is increased through the sorption of soil-borne DOC. (A) We conducted batch experiments using silt and differently stabilized (bare and citrate-coated (i.e. additionally charge stabilized) AgNP) AgNP at pH 6.5 and initial Ag concentrations ($c_0$) ranging from 30 to 500 µg/L. After 24 h of end-over-end-shaking and filtration (1.2 µm) the Ag concentration ($c_{Ag}$) was determined in the filtrate. The concentration of sorbed Ag was determined through the difference between $c_0$ and $c_{Ag}$. Results of both NP showed sorption curves with similar slopes, suggesting that particle charge does not control sorption. (B) Bare and citrate-stabilized AgNP were suspended in a centrifuged soil solution (cut-off 10 nm). Zeta potential and sorbed amounts of DOC were determined after 24 and 48 h. Results of bare AgNP showed high sorption after only 24 h as well as an increase in particle charge. During a period of 1.5 hours, time-resolved aggregation was determined by DLS measurements following the addition of (i) extracted soil solution and (ii) Ca-solution to obtain the same concentration as in the soil solution (1.5 mM Ca) to citrate-stabilized AgNP suspensions of various concentrations (0.5, 5, 10 mg/L). While at 0.5 and 5 mg/L Ag, the two treatments did not differ significantly in their particle size, at a Ag concentration of 10 mg/L AgNP exposed to soil solution showed lower particle sizes than AgNP exposed to Ca solution, suggesting that the stabilizing effect of DOC is relevant especially at high AgNP concentration.

**Keywords:** steric stabilization, charge stabilization, DOC sorption

# Mechanism and kinetics of iron nanoparticles oxidation in water: laboratory versus field study

*Jan Filip*[1], *František Karlický*[1], *Zdeněk Marušák*[1], *Josef Kašlík*[1], *Jaroslav Nosek*[2], *Monika Stavělová*[3], *Michal Otyepka*[1], *and Radek Zbořil*[1]

[1]Regional Centre of Advanced Technologies and Materials, Palacký University, Olomouc / Czech Republic

[2]Institute for Nanomaterials, Advanced Technologies and Innovation, Technical University of Liberec, Liberec / Czech Republic

[3]AECOM CZ s.r.o., Praha / Czech Republic

E-mail: jan.filip@upol.cz

## Abstract

A combined experimental and computational approach was employed in order to decipher mechanism and kinetics of the reaction of nanoscale zero-valent iron (nZVI) with water under both aerobic and anaerobic conditions. The reaction kinetics has been monitored at temperatures ranging from 25 to 80 °C mainly by $^{57}$Fe Mössbauer spectroscopy on frozen dispersion samples and the data were extrapolated to environmentally relevant temperature (10 °C) of typical groundwater. Both experimental and computational approaches indicate generally very slow kinetics, which is governed rather by chemical than physical reasons. The computations demonstrate two-step reaction involving two one-electron transfer processes: the first one is reaction $Fe + H_2O \rightarrow HFeOH$ (the rate limiting step), the second one is reaction $HFeOH + H_2O \rightarrow Fe(OH)_2 + H_2$. The primary reaction product identified experimentally is $Fe(OH)_2$, forming flat layered crystals extensively overgrowing nZVI particles. Then, ferrous hydroxide undergoes the secondary anaerobic transformation to the globular-shape magnetite ($Fe_3O_4$) nanoparticles according to Schikorr reaction. The observed reactions will be compared with field observations: reacted nanoparticles were extracted from groundwater at the locality contaminated by chlorinated hydrocarbons (VC, DCE, TCE and PCE) being treated by injected nZVI particles.

The authors gratefully acknowledge the support by the Technology Agency of the Czech Republic "Competence Centres" (project No. TE01020218).

**Keywords:** Zero-valent iron nanoparticles; Reaction with water; Reaction mechanism and kinetics; $^{57}$Fe Mössbauer spectroscopy; Quantum chemical calculation; Chlorinated hydrocarbons

# Reactivity, longevity and characteristic of nano zero valent iron particles for groundwater remediation

*André Matheis, Norbert Klaas, and Jürgen Braun*
VEGAS - Research Facility for Subsurface Remediation, University of Stuttgart, Stuttgart / Germany

E-Mail: andre.matheis@iws.uni-stuttgart.de, norbert.klaas@iws.uni-stuttgart.de,
juergen.braun@iws.uni-stuttgart.de

## Abstract

A relatively new method to remediate contaminants - mainly halogenated hydrocarbons - from groundwater is the use of nano-sized zero valent iron (nZVI) as suspension which is directly injected into a source zone. The iron reacts with the contaminants resulting in environmentally benign products.

To determine the degradation performance (reactivity) and longevity of nZVI particles, usually batch experiments are conducted. Such results, however, may not be directly transferable to the field scale since in batch experiments the contact between iron colloids and the contaminants is forced. In addition, the anaerobic corrosion as a side reaction is self-inhibiting due to the production of $OH^-$.

In field, however, flow of “fresh” contaminated water keeps the pH more stable. Thus, in systems with flow such as column experiments or field applications increased anaerobic corrosion is expected shortening the longevity. Moreover, hydrogen will be produced which potentially clogs the porous media and the anaerobic corrosion consumes nZVI which is no longer available for the reduction of contaminants.

Longterm column experiments have been performed to simulate a groundwater remediation under nearly natural conditions. The results show that anaerobic corrosion could be reduced by using $Ca(OH)_2$ to increase the pH, which is a suitable method to preconditioning the aquifer. The effect of $Ca(OH)_2$ on the longevity and reactivity of the nZVI will be discussed with focus on the consumption of nZVI due to anaerobic corrosion.

Within the BMBF-funded project NAPASAN, a new nZVI particle was developed. The NAPASAN particle was tested in comparison with other ZVI particles as a reference in experiments. These investigations of reactivity and longevity of zero valent iron particles show the performance of various particle-characteristics.

**Keywords:** nano-iron, reactivity, longevity, fate, groundwater, remediation

# Fate of natural and naturally modified engineered nano-particles related to in-situ remediation of soil and groundwater contamination

*Isam Sabbah, Yuri Haimov, and Niv Mor_*
Prof. Ephraim Katzir Department of Biotechnology Engineering, ORT Braude College, Karmiel / Israel

E-mail: isabbah@braude.ac.il

## Abstract

This research try to assess the transport and fate of natural and naturally-modified engineered NPs with respect to in-situ remediation of groundwater contaminants. To promise working with, rather than against, nature, the focus of recent research is on natural nanoparticles (NPs), modified NPs by using natural humic substances (HS) coatings.

Column experiments with sand, glass bead porous media as well as sandy loam soil from the Bet Dagan region (Hamra) were used to identify the mechanisms of transport and fate of NPs, and surface modified NPs with HS as either coating matrix or mobile liquid. CuO and TiO2 were selected to represent engineered nanoparticles.

Several experiments have been conducted to account for the breakthrough (BTC) of three HS sources in the studied porous media. By comparing the BTCs of HS to that of a non-sobbing tracer in the sand and glass columns, it was shown that the BTCs of the tracer and the two HS were very similar, indicating that sorption and retardation of both are insignificant. However, when applying the same procedure in a column of soil, the transport of HS was very limited showing high retardation. Also, we obtained that the source of the humics as well as the extraction method can significantly affect the mobility of humics through the soil.

As for the nano copper oxide and nano titanium oxide, the BTC show that these nanoparticles are not stable, where very rapidly an aggregation has been occurred even when using clean sand and glass beads as porous media. However involving HS leads to a significant enhancement of the transport of the engineered nano-particle.

These preliminary findings suggest that the transport of engineered and natural NPs (i.e., CuO, TiO2, HS) is not obvious and smooth, which claims more basic investigation for better understanding of their transport and fate.

**Keywords:** Humic substances, engineered nano-particles, transport, BTC, retardation

*Keynote*

## Transformations silver nanoparticles in urban wastewater systems

*Ralf Kaegi*[1]*, Basil Thalmann*[1]*, Andreas Voegelin*[1]*, and Eberhard Morgenroth*[1]
[1] Eawag: Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland

E-mail: ralf.kaegi@eawag.ch, basilius.thalmann@eawag.ch, andreas.voegelin@eawag.ch,
Eberhard.morgenroth@eawag.ch

### Abstract

Metallic silver nanoparticles (Ag-NP) are used as antimicrobial agents due to the well-known antimicrobial properties of $Ag^+$. In order to assess potential effects on the biology of the wastewater treatment plants (WWTP) and further on the downstream ecology, the transformations the Ag-NP during their transport in wastewater systems have to be addressed. Important transformation reactions include the sulfidation of Ag-NP which dramatically reduces the toxic response of the Ag-NP due to the limited solubility of the $Ag_2S$. However, it also has been demonstrated that partially sulfidized Ag-NP can have adverse effects on ecosystems. Therefore, kinetic considerations of the sulfidation reactions have to be taken into account.

We performed lab-scale, pilot-scale and full-scale experiments in sewer systems and WWTP using Ag-NP and AgCl-NP with different sizes (10 nm, 100 nm) and different coatings (citrate, PVP). In laboratory experiments, Ag-NP were reacted with CuS and ZnS, representing most relevant metal sulfides in urban waste and surface waters, to simulate conditions in oxic aqueous environments where free sulfides are quickly oxidized. Solid phases and solutions were analysed by a combination of bulk elemental (inductively coupled plasma mass spectrometry), particles specific (analytical electron microscopy) and element specific (X-ray absorption spectroscopy) methods. Results indicate a partial sulfidation of the Ag-NP and a complete sulfidation of the AgCl-NP during the transport in the sewer system. The sulfidation continues during the wastewater treatment and transformed Ag-NP are concentrated in the sludge. Kinetic sulfidation experiments revealed increasing sulfidation rates with decreasing Ag-NP size and increasing metal sulfide concentrations. Based on these experiments it is concluded that Ag-NP will be completely transformed into $Ag_2S$ within a period of hours to days also in the absence of free sulfide in oxic surface waters.

# Diffuse discharge of $TiO_2$ from landfills to the environment

*Michael Burkhardt*[1], *Silvan Stähli*[1], *Brian Sinnet*[2], *and Ralf Kägi*[2]

[1]Institute of Environmental and Process Engineering, HSR University of Applied Sciences, Rapperswil / Switzerland

[2]Department of Process Engineering, Eawag Institute of Aquatic Sciences and Technology, Dübendorf / Switzerland

E-mail: michael.burkhardt@hsr.ch, s1staehl@hsr.ch, brian.sinnet@eawag.ch, ralf.kaegi@eawag.ch

## Abstract

Significant quantities of nanomaterials are disposed with household and industrial water after combustion as thermally treated waste on landfills. The waste representing the end-of-life of products is classified as ashes or slags. The largest quantities of waste come from the construction industry and are considered as inert construction waste. In Switzerland, a variety of landfill types of different composition, amount, and leachate treatment exists. Although the vast mass of nanomaterials end up in landfills, hardly experimental studies have been published so far.

A monitoring study covering more than 20 landfills was conducted in the Canton Zürich. The landfill history was studied and leachate samples were collected. Temperature, $O_2$, redox-potential, and electrical conductivity were measured in the field. Particles, total suspended solids (TSS) and elemental concentrations were analysed in the lab using ICP-OES, total and dissolved organic carbon (TOC/DOC), and laser light diffraction (with, without sonication). Additionally, electron microscopy (SEM and TEM) coupled with energy dispersive X-ray (EDX) analysis was applied to study particles of filtered (0.2 μm) or centrifuged samples. Taking into account the water flux and the most prominent occurrence of Titanium identified, mass flow of $TiO_2$ was estimated for the point-of-discharge.

The results clearly show a widespread occurrence of fine particles in water samples of certain landfills and especially of $TiO_2$ in the nano-sized range. The concentrations reached up to a few milligrams titan per litre. TSS, conductivity and TOC proved to be good supporting indicators for the particulate content. Based on the morphology of the TiO2 particles detected with the electron microscope, these particles likely belong to the class of white pigments and possibly originate from weathering construction materials and residuals from waste. Compared with nano-release of WWTPs to aquatic environment, landfills may play a key-role in the mass flow of nanomaterials to the environment.

**Keywords:** discharge, landfill, titanium dioxide, waste

# In-situ groundwater remediation using nanoparticles: large scale experiments for investigation of transport and reactivity

*Kumiko Miyajima and Jürgen Braun*
Research Facility for Subsurface Remediation, IWS/VEGAS, University of Stuttgart, Stuttgart / Germany

E-mail: Kumiko.Miyajima@ies.uni-stuttgart.de, Juergen.Braun@iws.uni-stuttgart.de

## Abstract

NANOREM is a research consortium (EU, FP7) dedicated to develop in-situ groundwater remediation technologies. Nanoparticles are to be injected into the contamination to create a reactive zone in which contaminants degradation or immobilization will take place.

Currently, most predictions on particle transport are made based upon small scale column experiment. However obviously these predictions have to be incorrect (or very imprecise) since nature does not provide the perfect conditions these experiments are based upon.

In the Nanorem project transport (and reactivity) investigations are being conducted at variable scales including large scale containers with volumes of over 240 m³ (VEGAS, University of Stuttgart). These large scale upscaling investigations are indoor experiments at a field relevant scale with exactly controlled initial and boundary conditions and a highly disaggregated monitoring grid. They will realize not only a closed mass balance, but also maximum flexibility with contaminants and conclusions with respect of improving the real field sites.

Three container experiments are currently being set up: In a large aquifer (L x W x H = 9 x 6 x 4.5m) a BTEX source will be emplaced and remediated with nano Fe-oxides that enhance microbial degradation. In two containers (L x W x H = 6 x 1 x 3m each) aquifers will be contaminated with CHC and chemically reduced after the injection of different nZVI suspensions. The accurate description of the aquifers and the contaminant distribution as well as a dense monitoring system will allow for the testing of these nanoparticles materials and new monitoring equipment, furthermore provide the understanding of particles transport in porous media and knowledge on degradation products under field relevant conditions.

The presentation will give a short overview of the NanoRem consortium and will then address the investigation or transport and reactivity issues of nano-particles in large scale container experiments.

**Keywords:** nanoremediation, nano-particle transport, large scale experiment

## Mobility of stabilized silver nanoparticles in fissured sandstone

*Christoph Neukum*
Department of Engineering Geology and Hydrogeology, RWTH Aachen University, Aachen / Germany

E-mail: neukum@lih.rwth-aachen.de

### Abstract

For assessing the risk of contamination of groundwater resources due to engineered nanoparticles it is important to understand their transport and retention mechanisms in aquifers. The mobility of silver nanoparticles (AgNP) in saturated, variably fissured porous sandstone is investigated in laboratory experiments using drilling cores. Transport experiments with different types of sandstones are carried out under varied conditions to study the impact of electrolyte concentration, pore water velocities and mineralogy. Flow Field-Flow Fractionation (FlFFF) coupled to an UV detector is used for particle quantification concerning concentration and size distribution of the AgNP in the effluent samples. Experimental results are modelled using a state-of-the-art particle transport model considering two kinetic sites (attachment/detachment) model. The particle size distribution of the AgNP samples is quite uniform in each considered solute environment. The freshly prepared samples show hydrodynamic sizes between 40 and 45 nm while the primary particle size is 15 nm according to the manufacturer. The AgNP are stabilized with two different surfactants which enable stable AgNP suspensions even at high solute ionic strength. The transport experiments reveal large differences of the mobility and retention of AgNP in unfissured sandstone matrix, partly fissured matrix and in single fissured sandstone respectively. Mineralogy, pore sizes distribution and solute chemistry are important factors of the retention characteristics. Blocking of attachment sites and associated time dependent attachment of silver nanoparticles is another important transport process in the majority of the conducted experiments.

**Keywords:** silver nanoparticles, groundwater, contaminant transport

# Retention and remobilization of stabilized silver nanoparticles in soils

*Yan Liang[1], Scott A. Bradford[3], Jiri Simunek[4], Marc Heggen[2], Harry Vereecken[1], and Erwin Klumpp[1]*

[1]Institue of Bio- and Geosciences, Agrosphere (IBG-3), Research Center Jülich, Jülich / Germany

[2]Ernst Ruska-Centrum ER-C, Research Center Jülich, Jülich / Germany

[3]United States Department of Agriculture, Agricultural Research Service, U. S. Salinity Laboratory, Riverside / USA

[4]Department of Environmental Sciences, University of California, Riverside / USA

E-mail: e.klumpp@fz-juelich.de

## Abstract

Transport and retention of surfactant stabilized AgNP under environmentally relevant conditions was investigated by water-saturated columns packed with quartz sand and by undisturbed loamy sand soil columns with around 90% water saturation. The remobilization of retained AgNP from undisturbed soil was studied by changing the solution chemistry such as change of cation types and ionic strength reduction. Results of transport experiments in quartz sand and soil showed similar trends with regard to the effects of physicochemical factors, e.g., enhanced transport with decreasing solution IS, increasing AgNP input concentration and flow velocity. In contrast to the conventional filtration theory, retention profiles (RPs) in sand exhibited uniform, nonmonotonic, or hyperexponential shapes that were sensitive to physicochemical conditions, while significant retardation of AgNP breakthrough and hyperexponential RPs were observed in almost all the transport experiments with soil. Results from remobilization experiments indicated that further release of AgNP and clay from the soil was induced by cation exchange ($K^+$ for $Ca^{2+}$) that reduced the bridging interaction and IS reduction that expanded the electrical double layer. Transmission electron microscopy, energy-dispersive X-ray spectroscopy, and correlations between released soil colloids and AgNP indicated that some of the released AgNP were associated with the released clay fraction.

## References

Liang, Y., Bradford S.A., Simunek, J., Heggen M., Vereecken H., Klumpp E.: Retention and Remobilization of Stabilized Silver Nanoparticles in an Undisturbed Loamy Sand Soil. Environ. Sci. Technol., 47(21) (2013) 12229–1223.

Liang, Y., Bradford S.A., Simunek, J., Vereecken H., Klumpp E.: Sensitivity of the Transport and Retention of Stabilized Silver Nanoparticles to Physicochemical Factors. Water Research, 47 (2013) 2572-2582.

**Keywords:** silver nanoparticles, transport, retention, release, soil, column experiments

# The transport and impact of metal nanoparticles in soil

*Ishai Dror and Brian Berkowitz*
Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot / Israel

E-mail:ishai.dror@weizmann.ac.il

## Abstract

The fate, transport and mobility of nanoparticles in soil are strongly dependent on environmental conditions. In this study we present the effect of soil properties on the transport of silver nanoparticles (AgNPs) in a set of laboratory column experiments, using different combinations of size fractions of a Mediterranean sandy clay soil. AgNPs are shown to have high mobility in soil with outlet relative concentrations ranging from 30% to 70%, depending on experimental conditions. The AgNP mobility through the column decreases when the fraction of smaller soil aggregates is larger. An early breakthrough pattern was found for the AgNP but not observed for AgNPs in pure quartz columns nor for bromide tracer in soil columns, suggesting that early breakthrough is related to the nature of AgNP transport in natural soils. Micro-CT and image analysis used to investigate structural features of the soil, suggest that soil aggregate size strongly affects AgNP transport in natural soil. These findings point to the importance of AgNP–soil chemical interactions as a retention mechanism, and demonstrate the need to employ natural soils rather than glass beads or quartz in representative experimental investigations. It is further noted that little is known about the possible effects of nanoparticles on soil chemical, physical and biological properties. Here we show that although copper oxide nanoparticles (nCuO) had little impact on the macroscopic properties of the soil, they did cause changes to humic substance structure and affected the soil bacterial community composition. In particular, the nCuO was found to have a strong effect on bacterial hydrolytic activity, oxidative potential, community composition and size in Bet-Dagan soil. These results indicate that CuO NPs are potentially harmful to soil environments. Furthermore, the results suggest that the clay fraction and organic matter in different soils interact with the nCuO and reduce its toxicity.

**Keywords:** silver nanoparticles, copper oxide nanoparticles, soil, transport

# Transport and retention of engineered silver nanoparticles in natural soils

*Anika Braun, Christoph Neukum, and Rafig Azzam*
Department of Engineering Geology and Hydrogeology, RWTH Aachen University, Aachen / Germany

E-mail: braun@lih.rwth-aachen.de, neukum@lih.rwth-aachen.de, azzam@lih.rwth-aachen.de

## Abstract

The increasing production of engineered nanoparticles (ENP) and their widespread use in consumer products are raising concerns regarding the release of nanoparticles into the environment, their mobility and fate. Recent studies show uptake and toxic effects of ENP towards many organisms, thus indicating a potential for future contaminants. To assess the risk of a contamination of drinking water resources or soil ecosystems it is important to examine the mechanisms of nanoparticle transport and deposition in soils and aquifers, which are still only poorly understood.

Antibacterial silver nanoparticles (AgNPs) are the most commonly used nanoparticles. In this study we examined the transport of commercially available stabilised AgNPs through water saturated soil columns packed with a loamy sand and a silty loam, respectively. Relevant physicochemical parameters like flow velocity, ionic strength and valence of the background electrolytes were varied to examine their effect on nanoparticle transport. Concentration and particle size distribution of AgNPs in the column effluents were analysed with asymmetrical flow-field flow fractionation, which allows not only to determine the breakthrough concentrations of AgNPs, but also to identify aggregation processes that occurred during the transport through the soil matrix. The breakthrough curves of AgNPs were inversely fitted using an advection-dispersion equation with one kinetic site attachment/detachment model to establish transport models that describe the deposition processes quantitatively. Selected columns were analysed for AgNPs retained in the soil matrix. The depth profiles of deposited AgNPs were included into the inverse modelling, elucidating relevant mechanisms of particle deposition.

Under certain conditions AgNPs showed a high mobility in the loamy sand, which was restricted mainly by high ionic strengths of the background electrolyte and the presence of bivalent ions. Transport was strongly limited in the fine grained silty loam. Furthermore, no relevant indication for nanoparticle aggregation processes could be observed in the column effluents.

**Keywords:** engineered nanoparticles, groundwater, transport modelling

# A new approach to studying fate and transport of nanoparticles under unsaturated conditions

*Samuel Kwame Kumahor and Hans-Jörg Vogel*
Department of Soil Physics, Helmholtz Centre for Environmental Research – UFZ, Halle /Germany

E-Mail: Samuel.Kumahor@ufz.de

## Abstract

For natural colloids sorption onto air-water interfaces has been found. Not much is known about this effect for nanoparticles since most of existing work is done under saturated conditions and considering their specialized nature in terms of size for instance. However unsaturated transport experiments are difficult to conduct, because it is demanding to establish well defined conditions in terms of water-air distribution (and interfaces) along a flow path. We present a new experimental technique which solves this problem. We present preliminary results on the transport of surface modified silver nanoparticles at different pH, different flow rates and water contents.

# Oral Session

# Toxicity

*Thursday, March 13, 2014*
Room: Audimax

***Keynote***

## Nanoparticles in the aquatic environment

*Albert A. Koelmans*
Aquatic Ecology and Water Quality Management Group, Wageningen University / The Netherlands.
Institute for Marine Ecosystem Studies (IMARES), IJmuiden / The Netherlands

E-mail: bart.koelmans@wur.nl

### Abstract

Over the past years, our understanding of possible impacts of nanomaterials on aquatic systems has grown considerably. Fate models have evolved from steady state mass balance models to dynamic models that incorporate temporal and spatial detail and might be used for site specific assessments. The body of laboratory toxicity data is growing too. The first longer term effect studies have been performed, and even the first community studies have been published. Although often still provisional and prognostic by nature, several inferences on the actual impacts of nanomaterials may be made by combining the best available information on fate, exposure and effects.

This talk will first address the present state of the art in modeling the fate of nanomaterials on the system level. This includes a brief history of recent developments, some viewpoints on the different approaches to model the fate of nanomaterials, and some example scenario studies that show the potential of present models to accurately simulate retention and to assess exposure to aquatic biota.

Then some considerations on effect assessment will be presented, such as the ranges of the present effect thresholds observed in laboratory tests, the possibility to add ecological relevance by using species sensitivity distribution concepts for nanomaterials, and the value of *in situ* community field studies to calibrate laboratory test results.

Finally some though experiments regarding the risk assessment of nanomaterials will be presented, as well as some finalizing thoughts on major present unkowns and future challenges.

**Keywords:** nanomaterials, fate, exposure, effects, risks.

# Looking beyond standard testing of $TiO_2$ nanomaterials – consideration of solar radiation in the *Daphnia* sp. acute immobilization test

*Anne J. Wyrwoll, Petra Lautenschläger, Alexander Bach, Andreas Schäffer, and Hanna M. Maes*
Institute for Environmental Research, RWTH-Aachen University, Aachen / Germany

E-mail: Anne.Wyrwoll@rwth-aachen.de

## Abstract

Photoactive $TiO_2$ nanomaterials (nano-$TiO_2$) are used in a broad range of products and applications e.g. in waste water treatment. Photoactivity of the particles is induced by ultraviolet (UV) radiation leading to the formation of reactive oxygen species (ROS). ROS may induce oxidative stress in organisms. Therefore, we investigated the influence of solar radiation on the acute toxicity of different sized anatase $TiO_2$ materials (nanomaterials NM101, NM102 and non-nanoreference NM100; primary particle sizes: 7, 15, and 200 nm) to *Daphnia magna.*

*Daphnia* sp. acute immobilization tests (OECD 202, 48 h) were performed under laboratory light (LL) and simulated solar radiation (SSR; 280-1000 nm, UV irradiation: 2.5 mW/cm²) in 10fold diluted ISO medium. In an additional experiment the Ti concentration was measured in test vessels containing the previously determined EC50 concentrations. $TiO_2$ analysis was carried out with inductively coupled plasma optical emission spectroscopy (ICP-OES) after microwave assisted acid digestion of the water samples (0 h and 48 h).

Except for NM 101 (EC50 79.5 mg/L) no toxic effects were monitored under LL conditions. SSR induced toxicity was more pronounced for the nanomaterials NM 102 and NM 101 (nominal/measured EC50 0.53/0.09 and 1.28/0.24 mg/L) than for the non nano reference NM 100 (nominal/measured EC50 3.88/0.33 mg/L). We assume that differences in SSR induced toxicity are related to differences in photoactivity. The measured NM102 EC50 (90 µg/L) is close to the predicted environmental aquatic nano-$TiO_2$ concentration in the µg/L range. However, under natural conditions humic acids may have an influence on the ROS production by $TiO_2$ materials, thus it remains unclear whether NM102 poses a risk for the environment.

The present study shows the necessity of considering the photoactivity of nano and non-nano scale $TiO_2$ materials in their environmental risk assessment, e.g., by conducting ecotoxicity tests under solar radiation.

**Keywords:** nano-$TiO_2$, *Daphnia magna*, solar radiation

# Particle characteristic related effects of titanium dioxide nanoparticles on *Daphnia magna* and *Gammarus fossarum*

*Frank Seitz*[1], *Ricki R. Rosenfeldt*[1], *Sandra Schneider*[1], *Ralf Schulz*[1], *and Mirco Bundschuh*[1,2]

[1]Institute for Environmental Sciences, University of Koblenz-Landau, Landau / Germany

[2]Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Uppsala / Sweden

E-mail: seitz-f@uni-landau.de

## Abstract

Among different studies there is a high variability in the ecotoxicity of titanium dioxide nanoparticles ($nTiO_2$) – ranging from the mg to g/L level. As the underlying reasons remain unclear so far, the present study assessed the role of particle characteristics, i.e. initial particle size (55, 100, and 140 nm), surface area and crystalline structure composite (anatase and mixture of anatase-rutile) during 96-h acute toxicity tests with *Daphnia magna.* To furthermore evaluate whether benthic organisms may be similarly affected as pelagic filter feeders, amphipods (*Gammarus fossarum)* experienced comparable exposure conditions. The results of the present study revealed the initial particle size to trigger the ecotoxicity of $nTiO_2$ meaningfully: smaller initial particle sizes (55 nm) showed an up to 7-fold increased toxicity for *Daphnia* when compared to bigger ones (140 nm). Also the 100 nm particles of both products were less toxic than their smaller counterparts and more toxic than the largest (140 nm). Additionally the crystalline composite had an impact on the ecotoxicological potential of $nTiO_2$. This was displayed by an up to 4-fold increased 96-h $EC_{50}$ (*Daphnia*) for the composite mixture compared to pure anatase. Moreover, the particle surface area is of substantial importance for $nTiO_2$ toxicity: The particle surface normalized $EC_{50}$-values revealed significant differences for $nTiO_2 \leq 100$ nm and 140 nm sized particles. Furthermore, for different crystalline structure composites of the same initial particle size ($\leq 100$ nm) the particle surface normalized $EC_{50}$-values differed significantly, highlighting the role of particle surface in the context of ecotoxicological testing with daphnids. In contrast, the bioassays with *Gammarus* did not show any adverse effects of $nTiO_2$. Referring to the findings of the present study, the risk assessment of nanoparticles should urgently consider nanoparticle characteristics but also species' life history.

**Keywords:** invertebrates, crystalline structure, toxicity, Crustacea

# Factors triggering the combined toxicity of nanosized titanium dioxide and heavy metals

*Ricki R. Rosenfeldt[1], Frank Seitz[1], Johanna Höger[1], Ann-Cathrin Haigis[1], Ralf Schulz[1], and Mirco Bundschuh[1,2]*

[1] University of Koblenz-Landau, Campus Landau, Institute for Environmental Sciences, Landau/Germany

[2] Swedish University of Agricultural Sciences, Department of Aquatic Sciences and Assessment, Uppsala/Sweden

E-mail: rosenfeldt@uni-landau.de, seitz-f@uni-landau.de, hoeg7488@uni-landau.de, haig5188@uni-landau.de, schulz@uni-landau.de, mirco.bundschuh@slu.se

## Abstract

As an ingredient in many consumer products (e.g. paints and sunscreens) titanium dioxide nanoparticles ($nTiO_2$) may enter aquatic ecosystems via wastewater treatment plant effluents, where they probably co-occur with other stressors, such as heavy metals. The adsorption of free metal ions onto $nTiO_2$ surfaces may reduce their toxicity in some cases, due to their removal from the water phase. However, agglomerates of $nTiO_2$ – together with the adsorbed metal ions – may get actively ingested by filter feeding organisms, such as *Daphnia magna*, potentially enhancing the overall toxicity. In this context, the present study investigated shifts in copper (Cu) toxicity in presence versus absence of $nTiO_2$ after an interaction period (=aging) under different conditions. Thus, the influence of ionic strength and pH on the combined toxicity of $nTiO_2$ and Cu was assessed during 72-h acute toxicity test using *D. magna*. Briefly, the presence of $nTiO_2$ reduced Cu toxicity of the mixture aged in pure deionized water to an extent comparable to an unaged mixture of both stressors. The same was observed for an aging in test medium at pH 6. Contrary, 72-h aging in test medium at pH 8 lead to a 70% enhanced Cu toxicity following 48 h of exposure in presence compared to absence of $nTiO_2$. The supplemental analytics suggest that the test organisms finally ingest numerous $nTiO_2$ agglomerates together with high amounts of absorbed Cu ions. Hence, nanoparticle agglomerates may contribute meaningfully to the uptake and effects of other chemical stressors, while the environmental conditions during aging determine whether the toxicity of the mixture is increased or decreased by $nTiO_2$.

**Keywords:** mixture toxicity, aging, environmental relevance, carrier function

# The nanocomposite Carbo-Iron® shows no adverse effects on growth, survival and gene expression in zebrafish

*Mirco Weil[1], Tobias Meißner[2], Armin Springer[3], Wibke Busch[4], Dana Kühnel4, and Karen Duis[1]*
[1]ECT Oekotoxikologie GmbH, Flörsheim/Main / Germany
[2]Fraunhofer Institute for Ceramic Technologies and Systems, Dresden / Germany
[3]Centre for Translational Bone, Joint and Soft Tissue Research, Technical University Dresden, Dresden / Germany
[4]Helmholtz Centre for Environmental Research GmbH – UFZ, Leipzig / Germany

E-mail: m.weil@ect.de

## Abstract

Carbo-Iron®, a composite of active carbon and nano-$Fe^0$, was developed for degradation of halogenated hydrocarbons in contaminated aquifers. Potential ecotoxicological effects of Carbo-Iron in the aquatic environment were investigated with modified standard tests. Since beyond the contaminated zone $Fe^0$ can be expected to have oxidized to $Fe^{2+}$ or $Fe^{3+}$, oxidized Carbo-Iron was used in these tests.

Acute toxicity tests with zebrafish embryos and adults were performed according to an OECD draft test guideline (TG) and OECD TG 203. For a 36-day test with early life stages (ELS) of zebrafish (OECD TG 210), a flow-through system was adapted to the testing of Carbo-Iron suspensions. From each treatment, a subset of fish was transferred to control conditions 4 days before test end to investigate elimination of Carbo-Iron from the gut. Presence of particles in the test organisms and changes in microstructure of the gut were investigated with microscope methods. In all tests, particle size in stock and test suspensions was determined via dynamic light scattering. In the ELS test, particle concentration was measured weekly. Differential gene expression in zebrafish embryos exposed for 24 h to 10 mg/L Carbo-Iron was investigated in a microarray experiment.

At concentrations between 0.1 and 100 mg/L, Carbo-Iron had no influence on survival of embryos, larvae and adult fish, and on biomass and length in the ELS test. Carbo-Iron was detected in the gut of juvenile and adult fish at test end. The nanocomposite was no longer detectable in the gut of fish exposed to Carbo-Iron for 29 d with subsequent exposure to control water for 5 days. Expression of genes in zebrafish embryos was not significantly influenced by Carbo-Iron, confirming that no effects due to generation of reactive oxygen species, the primarily expected mode of action of iron composites and iron ions, occurred in the embryos.

**Keywords**: iron nanocomposite, flow through tests, gene expression, zebrafish

# Hazards of zero-valent iron nanoparticles used for soil and groundwater remediation

*Erik J. Joner*
Norwegian Institute for Agricultural and Environmental Research (Bioforsk), Ås, Norway

E-mail: Erik.Joner@bioforsk.no

## Abstract

Nanoparticles composed of zero-valent iron (nZVI) have been proposed as an inexpensive and efficient *in situ* remediation agent for dechlorination of organic pollutants in soil more than a decade ago. Still, its use has been far from as widespread as anticipated. The reason is partly the rising nano-scepticism seen during the same period. Regarding environmental implications, nZVI constitute a highly relevant type of nanoparticles, as they are reactive and will be spread intentionally in the environment in high amounts. A series of experiments on hazards of nZVI towards soil organisms have thus been conducted as parts of a national Norwegian project and a FP7 project (NanoRem) to determine potential hazards that this technology may imply for terrestrial and aquatic environments. Experiments included standardized and non-standardized tests and bioassays with plants, earthworms, collembolan, bacteria, algae and ostracods exposed to different concentrations and in the presence or absence of soils and other environmental matrices. The outcome of these studies indicates that one type of nZVI (produced by reduction of Fe salts using borohydride) may be highly toxic during a certain period after contact with soil and water, but that oxidation and ageing reduce the toxicity substantially(El-Temsah and Joner 2012b, a, 2013; El-Temsah et al. 2013). Other types of iron nanoparticles, including nZVI, are far less toxic, but also less efficient in dechlorination of organic pollutants. Column experiments indicate that nZVI is poorly mobile, but that transformation products like dissolved Fe(II) may cause adverse effects beyond the treatment zone. The implications of nZVI modifications with coatings that enhance particle mobility will be discussed, as will the associated environmental risks as modified by realistic exposure scenarios.

## References

El-Temsah YS, Joner EJ (2012a). Chemosphere 89:76-82.
El-Temsah YS, Joner EJ (2012b). Environmental Toxicology 27:42-49
El-Temsah YS, Joner EJ (2013). Chemosphere 92:131-137.
El-Temsah YS, et al. (2013) Plant and Soil 368:189–200.

**Keywords:** ageing, ecotoxicity, nZVI

# Impact of silver nanoparticles on bacterial biofilms – *monospecies* vs. natural biofilms

*Alexandra Grün*, *Constantin App, Andreas Breidenbach, Jutta Meier, and Werner Manz*
Institute for Integrated Natural Sciences, Department of Biology, University of Koblenz-Landau, Koblenz, Germany

E-mail: alexg@uni-koblenz.de, manz@uni-koblenz.de

## Abstract

The application of engineered silver nanoparticles (Ag NPs) in a wide range of consumer products finally results in their release into sewage systems and subsequently into the aquatic environment. Therefore bacterial biofilms as the natural life forms of microorganisms in natural watercourses may be impacted by Ag NPs leading to a potential impairment or loss of essential ecosystem functions ensured by natural biofilms. To elucidate potential effects of Ag NPs, *monospecies* biofilms of freshwater bacterium *Aquabacterium citratiphilum* cultivated under laboratory conditions were exposed to different sizes of citrate-stabilized Ag NPs (30 and 70 nm in size) in concentrations ranging from 600 to 2400 µg/L. Based on results from atomic absorbance spectroscopy (AAS) measurements a high uptake capacity for Ag NPs by the biofilms was determined. Biofilms' architecture characterized by gravimetric measurements showed a decrease in density of Ag NP's treated biofilms which correlated with remarkable loss in both cellular and EPS protein quantities. Furthermore, these interferences were accompanied with a decline in biofilm stability.

In order to obtain additional ecotoxicological insights, defined mesocosm studies were performed. Within the mesocosms featured by water and sediment from the river *Rhine*, riverine biofilms were cultivated from natural inoculum and exposed to 600 µg/L of Ag NPs (30 and 70 nm in size) for 14 days. Besides gravimetric, protein and chlorophyll *a* measurements, changes in the composition of the bacterial community were investigated. T-RFLP-fingerprint indicated that Ag NPs lead to an altered composition of the phylogenetical community structure in the biofilm. Additionally, data from16S-rRNA-clone libraries revealed that the phylogenetical alteration was coming along with a considerable displacement in distribution and abundance of bacterial taxa.

**Keywords:** bacterial biofilms; silver nanoparticles; riverine, ecosystem functions

## Silver nanoparticle uptake and growth inhibition in wheat

*David W. Britt*[1], *Christian O. Dimkpa*[2], *Joan E. McLean*[3], *Nicole Martineau*[2], *Richard Haverkamp*[4], *and Anne J. Anderson*[2]

[1]Department of Biological Engineering, Utah State University, Utah / USA

[2]Department of Biology, Utah State University, Utah / USA

[3]Utah Water Research Laboratory, Utah State University, Utah / USA

[4]School of Engineering and Advanced Technology, Massey University, Palmerston North / NZ

E-mail: david.britt@usu.edu, cdimkpa@usu.edu, joan.mclean@usu.edu, R.Haverkamp@massey.ac.nz, anne.anderson@usu.edu

### Abstract

Hydroponic plant growth studies indicate that silver nanoparticles (Ag NPs) are phytotoxic. In this work, the phytotoxicity of commercial Ag NPs (10 nm) was evaluated in a sand growth matrix. Both NPs and soluble Ag were recovered from water extracts of the sand after growth of plants challenged with the commercial product; the surface charge of the Ag NPs in this extract was slightly reduced compared to the stock NPs. The Ag NPs reduced the length of shoots and roots of wheat in a dose-dependent manner. Furthermore, 2.5 mg/kg of the NPs increased branching in the roots of wheat (*Triticum aestivum* L.), thereby affecting plant biomass. Micron-sized (bulk) Ag particles (2.5 mg/kg) as well as Ag ions (63 µg Ag/kg) equivalent to the amount of soluble Ag in planted sand with Ag NPs (2.5 mg/kg) did not affect plant growth compared to control. In contrast, higher levels of Ag ions (2.5 mg/kg) reduced plant growth to a similar extent as the Ag NPs. Accumulation of Ag was detected in the shoots, indicating an uptake and transport of the metal from the Ag NPs in the sand. Transmission electron microscopy indicated that Ag NPs were present in shoots of plants with roots exposed to the Ag NPs or high levels of Ag ions. Both of these treatments caused oxidative stress in roots, as indicated by accumulation of oxidized glutathione, and induced expression of a gene encoding a metallothionein involved in detoxification by metal ion sequestration. Our findings demonstrate the potential effects of environmental contamination by Ag NPs on the metabolism and growth of food crops in a solid matrix.

**Keywords:** silver, wheat, *Triticum aestivum* L., oxidative stress, growth inhibition

# Evaluation of the eco-toxicological relevance of silver nanoparticles in soil

*Christoph Emmerling and Mathias Hänsch*
University of Trier, Depart. Soil Science / Germany

E-mail: emmerling@uni-trier.de

## Abstract

This study aimed to evaluate the potential eco-toxicological risk of silver nanoparticles (AgNP) in soil. For this, a medium-term (2 to 6 months) microcosm experiment was conducted for which a commercially available AgNP product was used in an environmentally relevant concentration. Soil samples from a Fluvisol have been applied with activated sludge previously spiked with 55 µg AgNP $kg^{-1}$ soil. As controls, a sludge treatment with silver nitrate addition in the same range (55 µg $AgNO_3$ $kg^{-1}$ soil), a sludge treatment without silver addition and a treatment without sludge and silver additions were used. The background concentration of total amount of Ag in this soil was approx. 1 mg Ag $kg^{-1}$ soil. For evaluation purposes we analyzed microbial biomass C and N (MBC, MBN), microbial activity (respiration), enzyme activities (fluorescent micro-plate assay) and microbial community composition (phospholipid fatty acid markers). Microbial properties, i.e. MBC were significantly decreased with time in both silver treatments. In the AgNP treatment a further decrease of MBC accounted for 15 % relative to the $AgNO_3$ control treatment. Amounts of total PLFA, total bacteria, Gram-positive and Gram-negative bacteria as well as fungi were slightly decreased in the AgNP treatment. However, changes in microbial community composition were not significant. To the present state of knowledge, we carefully suggest a threshold level of AgNP in soil in a range of approx. 50 to 150 µg AgNP $kg^{-1}$ soil which might be occurred in quite a short period of 35 years of sewage sludge application based on calculations of annual change in AgNP concentration in sludge treated soils (Gottschalk et al., 2009).

**Keywords:** Silver nanoparticles, risk assessment, Activated sludge, Microbial biomass, Phospholipid fatty acids, threshold level

# Dispersion and stability of silver nanoparticles in different ecotoxicological test media

*George Metreveli*[1], *Frank Seitz*[2], *Alexandra Grün*[3], *Mirco Bundschuh*[2,4], *Ralf Schulz*[2], *Werner Manz*[3], *and Gabriele E. Schaumann*[1]

[1]Department of Environmental and Soil Chemistry, Institute of Environmental Sciences, University of Koblenz-Landau, Landau / Germany

[2]Department of Ecotoxicology and Environment, Institute of Environmental Sciences, University of Koblenz-Landau, Landau / Germany

[3]Institute for Integrated Natural Sciences, Department of Biology, University of Koblenz-Landau, Koblenz / Germany

[4]Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Uppsala / Sweden

E-mail: metreveli@uni-landau.de

## Abstract

In experiments investigating the ecotoxicological potential of engineered nanoparticles (ENPs), various test media with high salt concentrations and thus high ionic strength are typically used. At such high ionic strengths the particle agglomeration is usually promoted, leading to changes in nanoparticle size and morphology as well as to the reduction of particle concentration due to sedimentation. In addition, some test media contain dissolved organic matter (DOM) which can influence nanoparticle stability and impair their dissolution. Furthermore, the initial concentration of ENPs is a next critical factor, which can considerably influence the particle stability in the aqueous medium. This phenomenon, however, is often neglected in ecotoxicological investigations, i.e. during dose-response experiments. All of these can result in biased interpretation of experimental data. Moreover, our current knowledge on fate, transformation and stability of ENPs in ecotoxicological test media is not sufficient to allow a comparison of effects derived from different studies applying differing media. A first step into this direction is the development of detailed information about nanoparticle stability, transformation and dissolution in employed test media.

In the present study, agglomeration of citrate stabilised silver nanoparticles in different ecotoxicological test media was investigated. Furthermore, the release of silver from nanoparticles was characterised. Following test media were used: ASTM (applied for *Daphnia magna*), SAM-5S (applied for *Gammarus fossarum*), and R2A (applied for biofilm). An agglomeration of nanoparticles was observed in all test media. As expected, agglomeration was predominantly influenced by the concentration of divalent cations and increased in following order: R2A < SAM-5S < ASTM. Natural organic matter (humic acid and seaweed extract) stabilised nanoparticles only partly and the stabilising effect decreased with increasing equilibration time. An increase in the initial particle concentration from 100 µg/L to 10 mg/L resulted in their increasing agglomeration. Furthermore, a release of Ag in the fraction < 2 nm (comprising $Ag^+$ and ultrasmall $Ag^0$ particles) was detected in all ecotoxicological test media. The release of silver was influenced by media composition and presence of organic matter. In the presentation, we will discuss how the engineered nanoparticles are destabilised and transformed after dispersing in ecotoxicological test media. The present findings are crucial for better planning of the ecotoxicological experiments and for correct interpretation of gained toxicity data.

**Keywords:** engineered nanoparticles, stability, transformation, agglomeration

# Sonication of nanomaterials used in toxicological studies

*Tobias Meißner, Kathrin Oelschlägel, and Annegret Potthoff*
Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Dresden / Germany

E-mail: tobias.meissner@ikts.fraunhofer.de, annegret.potthoff@ikts.fraunhofer.de

## Abstract

Toxicological testing of nanomaterials often comprises the dispersion of nanoscaled powder in order to bring the particles into the test surrounding. Various dispersion approaches have been described in the literature, with the main differences between them being sonication method, the medium and additives used.

Five dispersion approaches were compared using the well-known $TiO_2$ P25. Three of the selected approaches were two- or multi-step processes consisting of dispersion in water followed by transfer to cell culture media, while the two other procedures include only the dispersion in water or in media. One approach was based on bath sonication, whereas the others used direct sonication through insertion of a probe into the sample. The main finding arising out of the comparison of the probe sonication methods was that the specific energy input played a crucial role in determining the achievable particle size. A low volume of liquid and a relatively low power in conjunction with a long pulsed dispersion time were found to be favorable for minimizing the side effects of ultrasonication like radical formation or material degradation. The resulting size in the cell culture media showed a strong dependence on the dilution method. Predilution with water before addition to the media prevented the agglomeration of the $TiO_2$ particles under physiological conditions.

The findings have been found can be transferred to ecotoxicological issues. Although electrolyte content is lower in ecotoxicological test water, agglomeration, as a result of low electrostatic stabilization, also can occur. If the nanomaterial is not already coated with polymeric compounds, organic stabilizer are often added in order to stabilize them. Effects of the dispersion in terms of ecotoxicological testing, particularly the ultrasound will be discussed.

**Keywords:** dispersion, sonication, particle characterization

# Oral Session

# Analytics

*Thursday, March 13, 2014*
Room: Audimax

***Keynote***

## Tuning Stability of Nanoparticle Suspensions by Polyelectrolytes

*Michal Borkovec*
Department of Inorganic and Analytical Chemistry, University of Geneva, Geneva, Switzerland

E-mail: michal.borkovec@unige.ch

### Abstract

Polyelectrolytes strongly influence the stability of colloidal suspensions, and this mechanism is highly relevant in environmental aquatic systems. Examples include removal of suspended particles by flocculation in waste-water treatment or stabilization of iron oxide or alumina particles by humic substances. Only recently, knowledge started to accumulate concerning the structure of adsorbed polyelectrolyte layers on oppositely charged surfaces and the resulting surface forces. Principal findings are that adsorbing polyelectrolyte lead to charge reversal and that the resulting layers are laterally heterogeneous and very thin (typically few nanometers). Interactions between these layers are principally controlled by electrostatic double-layer and van der Waals forces as described by the theory of Derjaguin, Landau, Verwey and Overbeek (DLVO). However, additional attractive non-DLVO forces are present, which are induced by lateral heterogeneities in the surface charge distribution (patch-charge attraction). The talk will review these recent developments and also highlight relevant state-of-the-art of experimental techniques (i.e., light scattering, reflectivity, quartz crystal microbalance, and atomic force microscopy).

**Keywords:** polyelectrolyte, adsorption, coagulation, aggregation

# ICP-MS-based characterization of inorganic nanoparticles – sample preparation and off-line fractionation strategies

*Anne-Lena Fabricius, Lars Duester, Björn Meermann, and Thomas Ternes*
Federal Institute of Hydrology, Department G2 - Aquatic Chemistry, Koblenz / Germany

E-mail: fabricius@bafg.de

## Abstract

Since the release of engineered nanoparticles (ENPs) into the environment has to be expected, the development and implementation of an appropriate risk assessment is inevitable. Therefore validated analytical methods are required, also implementable by non specialised laboratories like, e.g., in (eco)toxicological/environmental research or administrative services. Until now, the methods available for ENP characterization are often laborious, expensive, and/or demand specialized and trained operators.

Concerning metal-based ENPs, two main aspects are the quantification of the absolute mass concentration and of the "dissolved" fraction. Aiming to support the development of easily implementable analytical protocols, preferably simple methods were compared to determine (i) the total mass concentration of five metal-based ENP suspensions (Ag, $TiO_2$, $CeO_2$, ZnO, and Au; two sizes), and (ii) to quantify the "dissolved" fraction (defined as < 10 kDa).

(i) Concerning classical measurement approaches of inductively coupled plasma-mass spectrometry, it is still questionable if a direct application via nebuliser and spray chamber provides precise results. Asking if and which sample preparation is required, a comparison of microwave digestion, acidification and direct measurements was conducted. Except for Au 10 nm, the total concentrations determined by direct measurements were clearly lower than those measured after digestion (61.1 % for Au 200 nm to 93.7 % for ZnO), whereat acidification delivered better recoveries (89.3 % for ZnO to 99.3 % for Ag).

(ii) Comparing different off-line fractionation methods to determine the dissolved fraction of a silver ENP suspension, two filtration methods (ultrafiltration and tangential flow filtration), dialysis, ultracentrifugation and cloud point extraction were mainly appropriate with certain limitations, while dialysis and cloud point extraction cannot be recommended.

Even though ultrafiltration combined with microwave digestion could be identified as best practice, the results demonstrate that even for presumable simple analytical tasks the analytical tools available are not necessarily suitable for all nanomaterials.

**Keywords:** nanoparticle quantification, total concentration analyses, off-line fractionation, sample preparation, dissolved fraction, ICP-MS

# Stability and effects of natural coatings on engineered inorganic nanoparticles (EINP) investigated by surface enhanced raman spectroscopy (SERS)

*Melanie Kühn, Natalia P. Ivleva, Reinhard Niessner, and Thomas Baumann*
Technische Universität München, Institute of Hydrochemistry, München / Germany

E-mail: melanie.kuehn@tum.de

## Abstract

Fast growing fields of application for engineered inorganic nanoparticles (EINP) in industry and consumer products lead to rising emissions of EINP into the environment. Many EINP used in consumer products are often only weakly bound to their substrate promoting their release into the environment. Their transport in aquatic and terrestrial environments is controlled by the physical and chemical heterogeneity of the matrix along the flow path and the properties of the EINP themselves.

While EINP are well characterized concerning their field of applications, there is still a lack of knowledge regarding their stability and transport behaviour in the environment. EINP are likely to get coated with natural organic substances soon after release, which once formed influence stability and transport regardless of the core material. Therefore, it is crucial to characterize the surface properties and stability of the EINP and their possible coating materials to predict their behaviour under environmental conditions. However, analytical methods to characterize organic coatings on nanoparticles are scarce. One suitable tool is surface enhanced Raman spectroscopy (SERS). Silver nanoparticles are known to enhance the Raman signal of adsorbed or nearby substances significantly. Surface coatings on silver nanoparticles should therefore be accessible via the SERS effect.

Citrate as well as hydroxylammoniumchloride stabilized nanoparticles were coated with humic acid followed by a washing step. SERS results indicate the formation of a stable and stabilizing coating. Interaction of EINP with physical and chemical heterogeneous model surfaces is studied in microfluidic systems mimicking the flow paths in porous and fractured aquifers and with different coating materials.

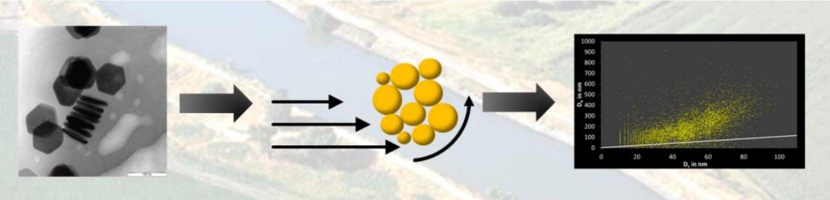
**Keywords:** Nanoparticle, organic coating, analyses, Raman microscopy

# Evaluation of hydrodynamic chromatography coupled with ICP-MS for the detection and quantification of inorganic colloids in environmental matrixes

*Allan Philippe, Denis Rakcheev, and Gabriele E. Schaumann*
Institute for Environmental Sciences, Department of Environmental and Soil Chemistry,
University of Koblenz-Landau, Landau / Germany

E-mail: philippe@uni-landau.de

## Abstract



Several scientists pointed out the lack of robust and efficient methods for the sizing and the quantification of engineered or natural colloids in the environment (e.g. Simonet *et al*., *Anal. Bioanal. Chem.* ,2009). This makes it difficult to investigate and to understand their environmental fate. Hydrodynamic chromatography (HDC) coupled with ICP-MS was shown to be a practical and efficient technique for the detection of inorganic nanoparticles in complex media (K. Tiede *et al., J. Anal. At. Spectrom.*, 2010). The claimed advantages of the method are its versatility, its relative simplicity, high recoveries and the possibility to combine sizing and quantitative analysis. However, the relation between environmental matrixes and the efficiency of HDC still needs to be investigated in order to know whether the method is suitable for analysis of nanoparticles in environmental samples. This talk aimed to report our advances in the development of a method using HDC-ICP-MS to analyse metal containing nanoparticles (Au, Ag, $TiO_2$…) in natural surface waters.

Using equipment and methods similar to those reported in the literature, we optimised flow rate, eluent composition and temperature and demonstrated the universality of the calibration method by measuring a wide range of calibrants with different densities and coatings. The combination of three detectors: UV-VIS, fluorescence, and ICP-MS, was especially helpful to resolve the matrix complexity for the analysis of Ag-nanoparticles and uranyl phosphates colloids in synthetic waters. Further experiments and discussions are about the unique possibilities offered by the coupling of HDC with single particle-ICP-MS. Powerful combination of detectors, versatility, and possibility to size and quantify inorganic nanoparticles simultaneously in complex matrixes are strong arguments a wide application of HDC in colloids analysis in environmental science.

**Keywords:** hydrodynamic chromatography, ICP-MS, agglomerates

# FTIR spectroscopy-based assessment of mobile goethite colloids after injection into a BTEX-contaminated aquifer - a field study

*Andreas Fritzsche*[1], *Julian Bosch*[2], *Thomas Ritschel*[1], *Matthias Händel*[1], *Rainer U. Meckenstock*[2], *and Kai U. Totsche*[1]
[1]Institute of Geosciences, Chair of Hydrogeology, Friedrich-Schiller-University Jena, Jena / Germany
[2] Helmholtz Zentrum München, Institute of Groundwater Ecology, Neuherberg / Germany

E-mail: a.fritzsche@uni-jena.de, julian.bosch@helmholtz-muenchen.de, thomas.ritschel@uni-jena.de, matthias.haendel@uni-jena.de, rainer.meckenstock@helmholtz-muenchen.de, kai.totsche@uni-jena.de

## Abstract

Colloidal iron oxides are promising agents for the remediation of organic contaminations in the subsurface. They overcome the generally low bioavailability of their non-colloidal counterparts in porous media and provide an enhanced reactivity. For the purpose of microbially mediated oxidative BTEX degradation, we injected a stable suspension of goethite nanoparticles into an anoxic aquifer under a former carbonization plant and refinery. The injected nanoparticles were intended to aggregate in dependence on the ambient ionic strength, which allowed for their controlled, i.e. sufficient but finite, mobility within the aquifer. With this novel approach, a well available and reactive electron acceptor, i.e. Fe(III) in goethite, is introduced into a designated aquifer compartment and is considered to stimulate the sustained activity of autochthonous microbial communities under anoxic conditions. However, a quantification of the goethite colloid spreading is required for estimating the dimension of the reactive zone in the aquifer and the amount of unutilized goethite, which is discharged from this zone. Nanoparticle toxicity also strongly depends on nanoparticle concentrations, emphasizing the need to quantify the concentrations of dispersed goethite to permit realistic toxicity predictions. Fe(III) analysis alone would fail owing to organic Fe(III) complexes and/or other dispersed iron oxides whose presence in the groundwater cannot be excluded a priori.

With this study, we propose an approach to estimate the amount of goethite in groundwater, which was sampled regularly before and after the injection event. Mathematic processing of ATR-FTIR spectra with positive matrix factorization identified several components, which agreed with organic (e.g. humic acids) and inorganic (e.g. gypsum, goethite) references. Shifts in the contribution of these compound-related components in the IR spectra provide information on actual compound distributions relative to a reference situation. Two months after injection, $Fe^{2+}$ was predominant in groundwater while goethite vanished, supporting the general functioning of the applied remediation technique.

**Keywords:** iron oxide nanoparticle, groundwater remediation

# Fine colloidal and nanoparticulate P, Fe, Al and C distribution in stream water of a German mountainous forest catchment

*N. Gottselig*[1]*, R. Bol*[1]*, V. Nischwitz*[2]*, H. Vereecken1, and E. Klumpp*[1]

[1]Institute of Bio- and Geosciences, Agrosphere (IBG-3), Jülich / Germany

[2]Central Institute for Engineering, Electronics and Analytics, Analytics (ZEA-3) Research Center Jülich, Jülich / Germany

E-mail: n.gottselig@fz-juelich.de, r.bol@fz-juelich.de, v.nischwitz@fz-juelich.de, h.vereecken@fz-juelich.de, e.klumpp@fz-juelich.de

## Abstract

Natural fine colloids and nanoparticles have the potential to encapsulate and bind nutrients. Their size range and composition is therefore relevant to understand the transport of essential nutrients like phosphorus in an aquatic ecosystem. The aim of the study was to characterize fine colloidal and nanoparticulate bound phosphorus of distinct hydromorphological areas in stream water from a forested experimental test site in a small headwater catchment. Asymmetric Flow Field Flow Fractionation (AF4) is a frequently used method when aiming at a separation and characterization of colloids in aquatic systems. It combines a large separation range (about 1 nm to 1 µm) with the possibility to couple various detection devices online. The separation is performed without a stationary phase in an open channel which is subject to a force acting perpendicular to the solvent flow and thus driving the fractionation. The fractionation occurs on behalf of diameter and diffusion rate of the particles.

AF4 coupled online to inductively coupled plasma mass spectrometry (ICP-MS) was applied for size resolved detection of phosphorus (P), iron (Fe), and aluminum (Al) in the fractions. Special focus was on P detection which is present at low concentrations (few µg/L) in many natural waters. Two distinct fractions (mean d~8 nm and ~150 nm) were detected and characterized. For the small size fraction, variations in P concentrations strongly correlated to the course of Al variations; in addition, high Fe presence in both fractions was accompanied by high P concentrations. The developed methodology enables for the first time to trace and conceptually define the inputs and source regions of fine colloidal and nanoparticulate fractions within a small river of a headwater catchment.

**Keywords:** field-flow fractionation, phosphorus, stream water, fine colloids, natural nanoparticles

# List of Posters

## Fate and Transport

**P1-01 Transport and retention of multi-walled carbon nanotubes in different porous media**
*Miaoyue Zhang, Daniela Kasel, Anne Berns, Harry Vereecken, and Erwin Klumpp*

**P1-02 Mobility of different $TiO_2$ nanomaterials and their influence on the mobility of copper or triclocarban in unsaturated soil columns**
*Carmen Nickel, Bryan Hellack, Stephan Gabsch, Michael Stintz, Hanna Maes, Andreas Schäffer, and Thomas Kuhlbusch*

**P1-03 Mobility and reactivity of iron oxide nanoparticles through biofilm coated porous media**
*Sneha Pradip Narvekar, and Kai Uwe Totsche*

**P1-04 The role of colloids and nanoparticles for the distribution of phosphorus in a forest soil**
*Anna Missong, Roland Bol , Volker Nischwitz, and Erwin Klumpp*

**P1-05 Effect of intermittent irrigation on silver nanoparticles transport in quartz sand and an undisturbed soil**
*Joanna Makselon, Eva Penssler, Yan Liang, and Erwin Klumpp*

**P1-06 Characterization of interactions between Carbo-Iron® and dispersants**
*Tobias Meißner, Theresa Klein, Jan Busch, and Annegret Potthoff*

**P1-07 Interaction of colloids and/or nanoparticles to the rock and mineral surfaces in the environment**
*Gopala Krishna Darbha, Johannes Lützenkirchen, and Thorsten Schäfer*

**P1-08 Migration of traffic-related palladium emissions in soils**
*Kerstin Leopold, Roland Schindl, and Lisa Malle*

**P1-09 Biochar aging in a long-term contaminated paddy soil and its reaction with soil metals**
*Rongjun Bian, Genxing Pan, Stephen Joseph, and Lianqing Li*

**P1-10 Hybrid sol-gel materials: a smart and cheap technology in environmental chemistry**
*F. Sannino, P. Pernice, A. Aronne, D. Pirozzi, E. Fanelli, and A. Piccolo*

**P1-11 Recovering magnetic nanoparticles after drinking water treatment**
*Konstantinos Simeonidis, Efthimia Kaprara, Nikolaos Andritsos, Theodoros Samaras, Georgios Vourlias, and Manassis Mitrakas*

**P1-12 Reactivities of two commercial nano iron particles for degradation of trichloroethene**
*Philipp Schöftner, Georg Waldner, Werner Lottermoser, and Thomas Reichenauer*

**P1-13 Nanocomposites – the benefits of enhancing or a problem with nanofillers**
*Lidia Tokarz, Marta Kijeńska, and Slawomir Pawlowski*

**P1-14 The influence of different geotechnically relevant amendments on the reductive degradation of TCE by nZVI**
*Peter Freitag, Philipp Schöftner, Georg Waldner, and Thomas G. Reichenauer*

**P1-15 Modelling the adsorption of methane on pure and Ag-doped multi-walled carbon nanotubes**
*Justyna Wrzosek-Jakubowska and Barbara Gworek*

**P1-16 Interactions of dissolved organic matter with inorganic colloids: a review**
*Allan Philippe and Gabriele E. Schaumann*

**P1-17 Sorption of engineered silver nanoparticles to environmental and model surfaces**
*Priya Mary Abraham, Thomas Baumann, and Gabriele E. Schaumann*

## Toxicity

**P2-01** **Ecotoxicological screening test of surface coated silver nanoparticles on multiple luminescent bacteria**
*Younjung Jung, Seungyun Baik, Jongwoon Kim, Hyunpyo Jeon, and Sanghun Kim*

**P2-02** **Integrating classical and molecular approaches to evaluate the impact of nanosized zero-valent iron (nZVI) on soil organisms**
*Maria Ludovica Sacca, Carmen Fajardo, Gonzalo Costa, Carmen Lobo, Mar Nande, and Margarita Martin*

**P2-03** **Application of zero-valent iron nanoparticles (nZVI) to metal immobilization in an acidic soil: ecotoxicological impact**
*M. Mar Gil-Díaz, Luis. T. Ortiz, Gonzalo Costa, Juan Alonso, M. Luisa Rodríguez-Membibre, Sebastian Sánchez-Fortún , Araceli Pérez-Sanz, Margarita Martín, and M. Carmen Lobo*

**P2-04** **Fate of CuO and ZnO nano- and micro-particles in the plant environment**
*David W. Britt, Christian O. Dimkpa, Joan E. McLean, Drew Latta, Maxim I. Boyanov , and Anne J. Anderson*

**P2-05** **Acute and chronic toxicity of aged titanium dioxide nanoparticles on *Daphnia magna***
*Simon Lüderwald, Frank Seitz, Ricki R. Rosenfeldt, Ralf Schulz, and Mirco Bundschuh*

**P2-06** **Implications of low titanium dioxide nanoparticle concentrations on the ecotoxicological potential of copper for *Daphnia magna***
*Theresa Schell, Ricki R. Rosenfeldt, Frank Seitz, Ralf Schulz, and Mirco Bundschuh*

## Analytics

**P3-01** **OECD protocols for a tiered determination of nanomaterial dispersions behaviour in different environmental media**
*Frank von der Kammer , Andreas Gondikas, Boris Meisterjahn, Kathrin Schwirn, Doris Voelker, and Thilo Hofmann*

**P3-02** **Speciation of phosphorus and colloidal Fe and Al (hydr)oxide complexes in different particle size fractions of an arable soil**
*Xiaoqian Jiang , Roland Bol, Sabine Willbold, and Erwin Klumpp*

**P3-03** **Separation and quantification of nanoparticles in aqueous samples using cloud-point extraction**
*Georg Hartmann and Michael Schuster*

**P3-04** **3D Distribution of retained silver particles in unsaturated porous media**
*Veronica L. Morales, Francisco J. Perez-Reche, Markus Holzner, Wolfgang Kinzelbach, and Wilfred Otten*

**P3-05** **Effects of surfactants and buffers on stability and electrophoretic mobility of gold nanoparticles**
*Denis Rakcheev, George Metreveli, and Gabriele E. Schaumann*

**P3-06** **Effect of silver nanoparticles on surface properties of bacterial biofilm - An AFM study**
*Sandra Barnikol, Alexandra Grün, Priya Mary Abraham, Dörte Diehl, Werner Manz, and Gabriele E.*

# Poster Session

# Fate and Transport

Room: Refectory

## P1-01

# Transport and retention of multi-walled carbon nanotubes in different porous media

*Miaoyue Zhang, Daniela Kasel, Anne Berns, Harry Vereecken, and Erwin Klumpp*
Institute of Bio- and Geosciences, Agrosphere (IBG-3), Jülich / Germany

E-mail: m.zhang@fz-juelich.de

## Abstract

The applications of multi-walled carbon nanotubes (MWCNT) will inevitably lead to their release into environment but little is known about the fate and behavior of MWCNT when exposed to environment. This study deals with the transport and retention of MWCNT in different porous media (quartz sands, silty loam and loamy sand) at different input MWCNT concentrations and low flow rates. MWCNT concentrations in the effluent and in the porous media were determined for breakthrough curves and retention profiles for all experiments. To more accurately understand the fate of MWCNTs, the breakthrough and deposition data collected were simulated by using HYDRUS-1D. In quartz sands, results demonstrate that normalized MWCNT transport increased with higher input concentrations and in coarser textured sand. The retention profiles showed that the majority of MWCNT retention occurred near the surface of the porous medium, especially for lower input concentrations and smaller sand sizes. In undisturbed soils, results revealed almost complete retention of functionalized MWCNT. More than 86% of MWCNT were recovered in the soil profile at conditions close to saturation. At lower water-saturation, MWCNT retention in the upper soil layers was enhanced. The co-transport of the pesticide Chlordecone in different porous media will also be discussed in this paper.

**Keywords:** multi-walled carbon nanotubes, column experiments, breakthrough curves, retention profiles, transport modelling, co-transport

## P1-02

# Mobility of different $TiO_2$ nanomaterials and their influence on the mobility of copper or triclocarban in unsaturated soil columns

*Carmen Nickel*[1], *Bryan Hellack*[1], *Stephan Gabsch*[2], *Michael Stintz*[2], *Hanna Maes*[3], *Andreas Schäffer*[3], *and Thomas Kuhlbusch*[1,4]

[1]Air Quality & Sustainable Nanotechnology, Institute of Energy and Environmental Technology (IUTA) e.V., Duisburg / Germany

[2]Institute of Process Engineering and Environmental Technology, Technische Universität, Dresden / Germany

[3]Institute for Environmental Research (Biology V), RWTH Aachen University, Aachen / Germany

[4]Center for Nanointegration, University Duisburg-Essen, Duisburg / Germany

E-mail: nickel@iuta.de

## Abstract

Nanomaterials are commonly used in many everyday life products. First studies indicated that nanomaterials are released from products during their life cycle. One exposure pathway to soil ecosystems is via the application of sewage sludge containing nanomaterials. In the presented study laboratory experiments were performed to investigate the mobility of different types of $TiO_2$ nanomaterials (P25, PC105 and UV Titan M262) in unsaturated soil systems, based on the OECD test guideline 312. The mobility in dependence on material characteristics (non-functionalised, functionalised, and crystalline structure) as well as the effect of different soil characteristics like clay content, pH-value, organic matter or cation exchange capacity on the adsorption and mobility behaviour was studied. Furthermore the carrier effect of P25 and the pollutant triclocarban or copper was investigated.

A low to no mobility of the tested nanomaterials was observed for all soil types, so probably the main part of the nanomaterial is absorbed effectively by the soils. Only for the with $Al_2O_3$ and dimethicone coated nanomaterial UV Titan M262 a transport was indicated based on ICP/OES measurements. But with SEM/EDX a transport of isolated $TiO_2$ agglomerates of all materials was detected in nearly all segments of the soils. It is conceivable that the bulk chemical analysis was not sensitive enough for the detection of this transport taking the natural Ti background up to 4 g/kg into account.

For the pollutants a tendency to a lower mobility was observed in the presence of P25. We hypothesize that the tendency to a lower mobility of copper as well as triclocarban can be explained by the adsorption onto the surface of P25. The low mobility of P25 leads therefore to a low mobility of the substance and in consequence to a higher exposure concentration for plants and animals living in the upper soil layers.

**Keywords:** $TiO_2$ nanomaterial mobility in soils, mobilisation of pollutants in the presence of nanomaterials, carrier effect, triclocarban mobility, copper mobility

## P1-03

# Mobility and reactivity of iron oxide nanoparticles through biofilm coated porous media

*Sneha Pradip Narvekar*, *and Kai Uwe Totsche*
Friedrich-Schiller-Universität Jena, Chair of Hydrogeology, Institute of Geosciences, Jena / Germany

E-mail: sneha.narvekar@uni-jena.de

## Abstract

Colloidal nanoparticles (CNP) such as organically modified Fe- and Mn-oxyhydroxides act as mobile geosorbents, thereby causing and affecting mobility and solubility of nutrients and pollutants. Stability and aggregation behavior control the mobility of CNP and depend on pH, ionic strength, and the presence of monovalent or divalent anions.

In natural systems like soils, sediments and aquifers, biofilms and extracellular polymeric substances (EPS) are an important component of the soil organic matter pool. Direct microbial effects, caused by redox reactions, may result in production of corrosive compounds like acids that may destabilize CNP. Recently, STXM and AFM studies showed that EPS and its components form submicron-sized, frequently patchy coatings of protein-rich and lipid-rich domains with iron oxide which will affect adsorption and co-precipitation.

The objective of our study was to quantify the effect of EPS and biofilm coatings on the colloidal stability, mobility and reactivity of hematite-CNP by column experiments in closed flow mode. The porous media was coated with *Bacillus subtillis* biofilm and with EPS extracted from *Bacillus subtillis*, respectively. The attachment efficiency of glass beads coated with biofilms decreased significantly from $21.03 \times 10^{-3}$ to $5.36 \times 10^{-3}$ on coating with biofilm. In uncoated porous media, Hematite CNPs are highly reactive and loses its colloidal stability and are deposited, whereas in coated porous media the nanoparticles are mobile and colloidally stable. The reactivity of hematite particles to the porous medium is reduced due to the masking of the reactive mineral surface sites of porous media with EPS and biofilm. EPS also brings about remobilization of about 8% of attached hematite.

**Keywords:** colloids, hematite, organic matter, microorganisms, transport.

## P1-04

# The role of colloids and nanoparticles for the distribution of phosphorus in a forest soil

*Anna Missong*[1]*, Roland Bol* [1]*, Volker Nischwitz*[2]*, and Erwin Klumpp*[1]

[1]Institute of Bio- and Geosciences, Agrosphere (IBG-3), Jülich / Germany

[2]Central Institute for Engineering, Electronics and Analytics, Analytics (ZEA-3) Research Center Jülich, Jülich / Germany

E-mail: a.missong@fz-juelich.de, r.bol@fz-juelich.de, v.nischwitz@fz-juelich.de, e.klumpp@fz-juelich.de

## Abstract

Colloids and nanoparticles (< 1 µm) play an important role for the binding, transport and distribution of nutrients like phosphorus in soil. High percentage of total phosphorus contents are associated to inorganic and organic fine colloids < 450 nm but the relevance is often neglected within this soil fraction. In forest soil, P is accumulated in surface and upper mineral layers but the lateral distribution of P in topsoil is highly inhomogeneous.

In this study samples from a coniferous forest were taken along a 2 m x 0.5 m grid with 30% slope. The effect of the slope position on the phosphorus distribution in the acidic topsoil samples was investigated. Water dispersible colloids (WDC), which represent the transportable colloid fraction, were extracted from field moist soil samples. Different size ranges (≤ 1µm, ≤ 450 nm, ≤ 100 nm) of WDC were separated and analyzed. The Field Flow Fractionation technique coupled online to UV-, DLS- detector and inductively coupled plasma mass spectrometry (ICP-MS) enabled a size resolved characterization of the colloidal fraction < 450 nm and their elemental composition (Fe, Al, P, Ca, Mn).

Colloids of surface- and mineral soil layers differed in colloidal composition and size distribution. Both layers show differences regarding particle bound phosphorus concentrations between the size range of 100 and 450 nm. The total phosphorus content does not correlate with slope whereby the colloidal bound phosphorus content increases with it.

The results confirm that P associated to colloids can be laterally translocated in soil and might be responsible for the heterogenic distribution of P in the topsoil layers. Differences in size depended phosphorus amounts indicate a preferential association of P to distinct colloid forms.

**Keywords:** colloid, phosphorus, soil, forest, transport

## P1-05

# Effect of intermittent irrigation on silver nanoparticles transport in quartz sand and an undisturbed soil

*Joanna Makselon, Eva Penssler, Yan Liang, and Erwin Klumpp*
Institue of Bio- and Geosciences, Agrosphere (IBG-3), Research Center Jülich, Jülich /Germany

E-mail: j.makselon@fz-juelich.de, e.penssler@fz-juelich.de, ya.liang@fz-juelich.de, e.klumpp@fz-juelich.de

## Abstract

Silver nanoparticles (AgNP) find a wide application area due to their antibacterial property. Thus, knowledge of the transport and retention of AgNP in soil is needed for risk assessment.

To investigate the transport behavior of stabilized AgNP, column and lysimeter experiments were performed. Column studies with quartz sand (water saturated) and undisturbed soil (90% water saturation) were conducted at constant and intermittent irrigation, respectively. A long-term lysimeter experiment was performed at intermittent irrigation and low water content. To determine breakthrough curves and retention profiles of AgNP, Ag concentrations were determined by ICP-MS both in the effluent and the packing.

Transport experiments in undisturbed soil column showed significant mobility of AgNP. The transport of AgNP in soil increases with higher input concentration, flow velocity and decreased ionic strength. AgNP transport in a long-term lysimeter experiment showed no significant breakthrough after one year. The retention profile indicated that most of the applied AgNP were retained in the upper soil layer. The results from quartz sand and undisturbed soil column experiments at intermittent irrigation will be compared to the lysimeter data to better understand the effect of intermittent irrigation on AgNP transport.

**Keywords:** silver nanoparticles, transport, intermittent irrigation, soil, column experiments

## P1-06

# Characterization of interactions between Carbo-Iron® and dispersants

*Tobias Meißner*[1], *Theresa Klein*[1], *Jan Busch*[2], *and Annegret Potthoff*[1]
[1]Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Dresden / Germany
[2]Institute for Earth and Environmental Science, University of Potsdam, Potsdam / Germany

E-mail: tobias.meissner@ikts.fraunhofer.de, janbusch@uni-potsdam.de, annegret.potthoff@ikts.fraunhofer.de

## Abstract

Carbo-Iron® is a novel nano-structured composite material made of zero-valent iron and activated carbon that is used for dehalogenation of contaminated groundwater. For an optimal application of Carbo-Iron, a high mobility within the contaminated aquifer is desirable. Therefore, dispersants are applied in order to enhance the stability of the nanomaterial and to avoid agglomeration of them.

Carboxymethyle cellulose (CMC) was suitable to stabilize Carbo-Iron. Zeta potential measurements, analytical centrifugation as well as quantitative adsorption experiments were performed to analyse the interactions between Carbo-Iron and CMC. The optimum amount of CMC was determined in order to ensure sufficient stability of Carbo-Iron suspensions. Moreover, column experiments were performed in inert porous media with addition of different amounts of CMC. Results show increased breakthrough levels with higher relative CMC concentrations. At concentrations lower than 2.5 wt.-% CMC, breakthrough is decreased compared to higher concentrations which is in good accordance to the findings of the zeta potential and centrifugation experiments.

Secondly, the influence humic acids on the system Carbo-Iron/CMC was investigated, because humic acids are known for their high affinity for adsorption and their acting as natural dispersant. The loading of Carbo-Iron with humic acid is about three times higher than with CMC, but the suspension stability of Carbo-Iron with humic acid is lower compared to Carbo-Iron with CMC. Moreover, adsorption of both dispersants increases with increasing water hardness. Regarding the technical application, suspended Carbo-Iron with already adsorbed CMC is injected into the aquifer. In this case, it adsorbed as much humic acid on Carbo-Iron with previously CMC as on CMC-free Carbo-Iron. Additional IR measurements show that humic acid cannot replace already adsorbed CMC which means that Carbo-Iron particles remain stabilized by CMC. This is of importance for the applicability as the stability of Carbo-Iron/CMC is not negatively affected by occurring humic acids.

**Keywords:** iron nanocomposite, adsorption, dispersant, particle characterization, column experiments

## P1-07

# Interaction of colloids and/or nanoparticles to the rock and mineral surfaces in the environment

*Gopala Krishna Darbha, Johannes Lützenkirchen, and Thorsten Schäfer*
Institute for nuclear waste disposal, Karlsruhe Institute of Technology, Eggenstein Leopoldshafen / Germany

E-mail: gopala.darbha@kit.edu

## Abstract

In nature, mineral colloids are ubiquitous and have an ability to sorb metal (toxic) ions on their surface and transport contaminants along with them. In this context, it is very important to understand their interaction with other mineral surfaces. Interaction of colloids ($Al_2O_3$, $SiO_2$) and nanoparticles ($TiO_2$) with rock and mineral surfaces was investigated by colloid probe technique (AFM) and conventional electrokinetic method under varying chemical conditions. With increasing pH (>6), as expected, a decrease in interaction forces between $Al_2O_3$ and $SiO_2$ particles with mineral surfaces (plagioclase, K-feldspar, quartz, biotite) was observed. Though $Al_2O_3$ and $SiO_2$ particles have similar adhesion forces towards mineral surfaces, $SiO_2$-K-feldspar and $Al_2O_3$-biotite are found to be higher compared to other colloid-mineral interactions. At pH=5, except for quartz, with an increase in [Eu(III)], the adhesion forces are ~6 times higher for $SiO_2$ towards minerals compared to $Al_2O_3$. Interestingly, a change in the magnitude of adhesion forces for four alumina particles of similar size vs a smooth biotite was observed, which is attributed to the rough features (of ~50 nm range) along colloidal particle verified by SEM and AFM.

In another study, the charging properties and interactions of $TiO_2$ nanoparticles (~10 nm) with silica colloids (<800 nm) was investigated. The electrokinetic and HRTEM measurements show, even under electrostatically unfavourable conditions (pH=8) where both surfaces are negatively charged, a significant amount of $TiO_2$ nanoparticles were sorbed on the surface of silica substrate in aqueous solutions. Upon the addition of $TiO_2$ nanoparticles to the streaming potential measurement setup with quartz (001) plane substrates resulted in a shift of IEP from negative value to 5. The AFM pictures of $TiO_2$ deposits on the quartz crystal further supports the irreversible deposition. The strong interaction of $TiO_2$ nanoparticles with silica suggests that the silica colloids are carriers of these purely inorganic nanoparticles.

**Keywords:** Colloid or nanoparticle interaction, adhesion forces, mineral surfaces, unfavourable electrostatic conditions, colloid probe technique

## P1-08

# Migration of traffic-related palladium emissions in soils

*Kerstin Leopold, Roland Schindl, and Lisa Malle*
Institute of Analytical and Bioanalytical Chemistry, University of Ulm, Ulm / Germany

E-mail: Kerstin.leopold@uni-ulm.de

## Abstract

Palladium (Pd) has excellent catalytic activity and is therefore widely used in car exhaust-gas catalytic converters. Due to abrasion several hundred ng Pd per kilometre can be emitted together with the exhaust. About 90% of these emissions are particulate matter varying in size from low µm to nm scale; however, it is believed that up to a third are fine particles of a few nm in diameter. Several monitoring studies prove the accumulation of Pd in different environmental compartments over the last decades and exposure studies suggest high bioavailable, phytotoxicity, and allergenic potential. Therefore, our studies aim at the understanding of transport and fate of traffic-related Pd emissions in the environment. In the presentation we will summarize our results obtained from investigation of roadside soil samples and model experiments for migration of Pd in soil. In particular, we will present depth profiles for Pd distribution in several infiltration basins. Highest Pd concentrations of more than 100 µg $kg^{-1}$ were found in the top layers, however, even in a depth of 30 cm several µg $kg^{-1}$ were detected. This finding gives evidence to considerable transport of Pd in the soil, since natural background values are expected to be an order of magnitudes lower. Therefore, model experiments were performed to enlighten transport mechanism and mobile Pd species in the soil. For this purpose, palladium(II) nitrate, non-coated Pd nanoparticles (Pd-NPs) or citrate-coated Pd-NPs, respectively, were applied onto different model columns, which were eluted with a defined volume of water. Fractions were collected and subsequently analysed for Pd showing that the mobility of Pd species follows the order citrate-coated Pd-NPs >>> non-coated Pd-NPs > Pd(II). The same trend was observed applying sequential extraction on soil samples spiked with known concentrations of these Pd species. In conclusion, all experiments suggest that coated Pd-NPs have high mobility in soils.

**Keywords:** traffic-related Pd emissions, palladium nanoparticles, migration in soil, Pd depth profiles of infiltration basins

## P1-09

# Biochar aging in a long-term contaminated paddy soil and its reaction with soil metals

*Rongjun Bian*[1]*, Genxing Pan*[1]*, Stephen Joseph*[1,2]*, and Lianqing Li*[1]

[1]Institute of Resources, Ecosystem and Environment of Agriculture, Nanjing Agricultural University, 1 Weigang, Nanjing / China

[2]School of Materials Science and Engineering, University of New South Wales, Sydney / Australia

E-mail: bianrongjun8806@163.com, pangenxing@aliyun.com

## Abstract

Biochar is an organic carbon-rich material that is produced via pyrolysis of agricultural bio-waste under an oxygen-limited environment. Biochar has received increasing attention as a carbon-negative and as an effective approach for soil improvement. In addition, many studies had confirmed that biochar can be applied for environmental remediation. Most of previous studies were conducted either in pot or microcosmic experiment or in short term mostly 1-2 year field experiment, focusing generally on the changes of biochar properties in nature soil. In the present study, a three year field experiment was conducted in a long-term contaminated paddy to determine the effect of biochar on soil heavy metals retention and the aging process of biochar in soil. The result indicated that biochar consistently and significantly increased soil pH, total organic carbon and decreased soil extractable Cd and Pb over the 3 year. We separated the biochar particles from the experiment field and compare the changes in surface functional groups and elements composition with microscopic examination. The XPS result showed the aged biochar have higher oxygen concentrations (O=C-O, N-C-COOH) but less carbon content, compared to the fresh biochar particles. The elements content in biochar particle surface, analyzed by LA-ICP-MS, indicated that aged biochar contained much higher levels of toxic metals (Cd, Pb, Al, As) but less nutrient elements (Mg, K, P) than fresh biochar particles. This could evidence that biochar could be a nutrient supplier and toxic metal stabilizer. The nanostructure of biochar particle and soil mineral compounds, measured by a high-resolution TEM-EDS, indicated that there was several different nano-phases formed through diffusion of soil solution containing cations and precipitation and/or reaction with the functional groups on the pore surface. This study demonstrated that the character of biochar was stable in soil and a consistent effect of biochar on soil heavy metal immobilization.

**Keywords:** biochar, soil remediation, aging, surface character, nanostructure

## P1-10

# Hybrid sol-gel materials: a smart and cheap technology in environmental chemistry

*F. Sannino[1,3], P. Pernice[2], A. Aronne[2], D. Pirozzi[2], E. Fanelli[2], and A. Piccolo[3]*

[1]Dipartimento di Agraria, Università di Napoli “Federico II”, Portici / Italy

[2]Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione industriale, Università di Napoli “Federico II”, Napoli / Italy

[3]Centro Interdipartimentale di Ricerca sulla Risonanza Magnetica Nucleare per l’Ambiente, l’Agro-Alimentare ed i Nuovi Materiali (CERMANU), Università di Napoli “Federico II”, Portici / Italy

E-mail: fsannino@unina.it, pernice@unina.it, anaronne@unina.it, dpirozzi@unina.it, efanelli@unina.it, alpiccol@unina.it

Research and development of novel hybrid materials with extraordinary properties has become one of the most expanding fields in recent years. Hybrid materials are raising a growing interest, as they offer the possibility of combining the reactivity of the organic components with the mechanical, thermal and structural stability of the inorganic framework, enabling a large range of applications such as green energy production, and environmental remediation.

In this study both the sorption and the intrinsic catalytic properties of a class II hybrid sol-gel zirconia (HSGZ) material are exploited in order to remove from aqueous solutions two different pollutants: 4-chloro-2-methylphenoxyacetic acid (MCPA), a phenoxy acid herbicide, and naphthalene (NAP), a typical two-ring polycyclic aromatic hydrocarbon (PAH). They both can be used as model compounds to set a new degradation strategy.

The structure of HSGZ can be described as a polymeric network of zirconium oxo clusters, on the surface of which large part of $Zr^{4+}$ ions are involved in strong complexation equilibria with acetylacetonate ligands.

The removal of pollutants was found to occur by a two-step mechanism in which a fast adsorption is followed by a degradative process leading to the complete pollutant removal.

In view of the extraordinary removal performance of this material, its oxidative capabilities into polymerization of soil humic superstructures have also investigated.

The significant reduction observed in soil respiration after reaction with HSGZ material, due to larger microbial recalcitrance acquired by the polymerized soil organic matter, may potentially facilitate carbon sequestration in soil and reduce the $CO_2$ emission thus representing a great challenge.

**Keywords:** hybrid sol-gel material; pollutant removal; carbon sequestration.

## P1-11

# Recovering magnetic nanoparticles after drinking water treatment

*Konstantinos Simeonidis*[1], *Efthimia Kaprara*[2], *Nikolaos Andritsos*[1], *Theodoros Samaras*[3], *Georgios Vourlias*[3], *and Manassis Mitrakas*[2]

[1]Department of Mechanical Engineering, University of Thessaly, Volos / Greece

[2]Department of Chemical Engineering, Aristotle University of Thessaloniki / Greece

[3]Department of Physics, Aristotle University of Thessaloniki / Greece

E-mail: ksime@physics.auth.gr, mkaprara@yahoo.gr, nandrits@uth.gr, theosama@auth.gr, manasis@eng.auth.gr

## Abstract

Iron-based nanoparticles have been recently studied as potential agents for the removal of heavy metals from aqueous solutions capable to reduce concentrations below the regulation limits for drinking water[1,2]. Their efficiency lies on their selective affinity to some contaminants (arsenic), their potential to reduce some other (hexavalent chromium) and, in any case, their reactivity introduced by high specific surface area. However, application of nanoparticles in real-scale water treatment plants is restricted by difficulties related to technological limitations and unsuccessful separation after use. In particular, the low dimensions of nanoparticles demand a different setup than typical column beds to ensure adequate contact with water while their possible dispersion in treated water requires a sequential filtration step which is rather expensive and insufficient to handle large particle quantities. In an effort to suggest a way for the facile and low-cost adoption of nanoparticles in water treatment, this study deals with the development of a continuous flow apparatus including a Cr(VI) removal stage by dispersing $Fe_3O_4$ nanoparticles followed by a highly-efficient separation process based on the flow of treated water through an external magnetic field. This approach combines the significant ability of $Fe_3O_4$ nanoparticles to reduce and capture Cr(VI) with their enhanced magnetic properties that allow easy recovery by magnetic forces. The system consists of a continuous flow stirring reactor with proper contact time in serial connection with an outflowing horizontal tube placed between parallel permanent magnets.

The research project is implemented within the framework of the Action “Supporting Postdoctoral Researchers” of the Operational Program "Education and Lifelong Learning" (Action’s Beneficiary: GSRT), and is co-financed by the European Social Fund and Greek State.

## References

[1] K. Simeonidis et al., Chem. Eng. J., 168 (2011) 1008.
[2] K. Simeonidis et al., EPJ Web of Conferences, 40 (2013) 08007.

**Keywords:** magnetic separation, nanoparticles, drinking water treatment

## P1-12

# Reactivities of two commercial nano iron particles for degradation of trichloroethene

*Philipp Schöftner*[1], *Georg Waldner*[1], *Werner Lottermoser*[2], *and Thomas Reichenauer*[1]
[1]AIT Austrian Institute of Technology GmbH, Tulln a.d. Donau / Austria
[2]Salzburg University, FB Materialforschung und Physik, Salzburg / Austria

E-mail: philipp.schoeftner.fl@ait.ac.at, georg.waldner@ait.ac.at, werner.lottermoser@sbg.ac.at, thomas.reichenauer@ait.ac.at

## Abstract

Zero valent iron (ZVI) is capable of remediating numerous contaminants. Reaction characteristics of ZVI particles differ between particle types hence particle properties and reaction characteristics of novel, hardly investigated, commercially available, nanoscale Nanofer Star, Nanofer 25 and Nanofer 25S particles were investigated in batch experiments and compared with previously often used, no longer produced RNIP particles. Trichloroethene (TCE) was used as model substance for volatile chlorinated hydrocarbons. Particle characteristics were determined using SEM (scanning electron microscopy), TEM (transmission electron microscopy), Mößbauer spectroscopy and XRD (X-ray diffraction). Surface area normalized reaction constants for TCE degradation over RNIP particles were 6 times higher than with Nanofer Star particles and the reaction was much more selective with respect to TCE. Electrons that were released by oxidation of RNIP particles reacted mainly with the target contaminant TCE whilst Nanofer particles oxidized at nearly 100 % under formation of $H_2$ by reduction of $H^+$. Undesired reaction to $H_2$ caused reduced Nanofer particle longevity due to high oxidation rates. Between Nanofer particles only minor differences were observed. Differences in sulfur content between particles may be an important reason for differences in reactivity due to the concomitant existence of hydrophobic and hydrophilic sites. Furthermore combination of Nanofer particles with microbes that can utilize $H_2$ for dehalorespiration may pose an advantageous field of application of Nanofer particles.

**Keywords:** zero valent iron, TCE, Nanofer, RNIP, VOC, remediation,

## P1-13

# Nanocomposites – the benefits of enhancing or a problem with nanofillers

*Lidia Tokarz*[1]*, Marta Kijeńska*[1]*, and Slawomir Pawlowski*[2]
[1]Institute of Environmental Protection – National Research Institute, Warsaw / Poland
[2]Industrial Chemistry Research Institute, Warsaw / Poland

E-mail: lidia.tokarz@ios.edu.pl

## Abstract

The technological development in different areas of industry resulted in the introduction to the environment of a large group of substances called „emerging contaminants" (ECs). This is a wide group of substances extraneous for the environment but of predicted high biological activity like hormones, pesticides, surfactants etc. From the point of view of plastics, widely use for packagings, the most important environmental pollutants are nanoparticles. The recent studies concern the applications of nanoparticle reinforcers to almost all types of polymers, from widely used polyolefins to advanced engineering polymers. Polyoxymethylene (POM) nanocomposites will be considered. POM is an engineering polymer implemented on the large scale especially in automotive industry and fancy goods. The benefits of introducing nanofillers to POM are outside discussion – improved mechanical properties result in much wider area of practical application. However there appears a problem of the storage of the products containing reinforced POM after the end of live and the controlling of their behaviour during landfilling. In the case of thin profiles or films the "sweating " to the surface of molded particles can happen so it‘s very important on monitoring the process. The paper presents the results of research of behaviour of POM nanocomposites. As nanofillers silica fumed, layers structures and hybrid structures core-shell type are used On the basis of the coefficient of static friction, PLM, SEM the environmental safety profiles were determined.

**Keywords:** polyoxymethylene, nanofillers, environmental safety

## P1-14

# The influence of different geotechnically relevant amendments on the reductive degradation of TCE by nZVI

*Peter Freitag*[1], *Philipp Schöftner*[2], *Georg Waldner*[2], *and Thomas G. Reichenauer*[2]
[1]Keller Grundbau Ges. mbH, Wien / Austria.
[2]AIT Austrian Institute of Technology GmbH, Tulln a.d. Donau / Austria.

E-mail: p.freitag@kellergrundbau.at, philipp.schoeftner.fl@ait.ac.at, georg.waldner@ait.ac.at, thomas.reichenauer@ait.ac.at

## Abstract

Trichloroethene (TCE) was widely used as a cleaning and degreasing agent. Companies applying these agents were often situated in built up areas, so spillage led to contaminated sites which now can only be remediated using in situ techniques. The situation is complicated by the fact that TCE seeps through ground water bodies forming pools at the bottom of the aquifer.

When reacting with TCE, nanoscale zero valent iron (nZVI) can lead to complete reductive dechlorination. The difficulty is to bring nZVI in contact with the pollutant. Attempts using passive insertion into the groundwater via wells yielded mixed results: nZVI coagulates, sediments and adsorbs on the matrix of the aquifer. Also, in inhomogeneous aquifers a passive application of nZVI can be difficult, due to existence of preferential flow paths.

A possible solution is the physical in situ mixing of ZVI into the contaminant source, e.g. via jet grouting, using a high pressure slurry jet consisting of water and geotechnical additives (“binders“), to mix and compact zones (“columns“) in soil. These columns are commonly used to solve foundation problems.

This paper examines the TCE degradation reaction with nZVI in presence of binders, which are necessary as the subsoil structure is rearranged during the jetting process, leading to subsidence on the surface. In batch experiments, we tested the effects of concresole, bentonite, zeolithe, fly ash, slag sand and cement on the kinetics of TCE degradation by nZVI. The degradation of TCE was measured using headspace GC analysis. Additional experiments were conducted to investigate the interaction between binders and TCE or nZVI.

Our conclusion is that jet grouting could be well suited for the delivery of nZVI to TCE contaminated source zones. Currently, soil column experiments and large-scale experiments in test facilities are performed to validate the scale-up strategy.

**Keywords:** zero valent iron, TCE, remediation, Nanofer, additives

## P1-15

# Modelling the adsorption of methane on pure and Ag-doped multi-walled carbon nanotubes

*Justyna Wrzosek-Jakubowska and Barbara Gworek*
Institute of Environmental Protection - National Research Institute, Warsaw / Poland

E-mail: justyna.wrzosek@ios.edu.pl, barbara.gworek@ios.edu.pl

## Abstract

Gas adsorption on carbon nanotubes is an important issue for both fundamental research in nanotubes and their technical applications for environmental protection. Carbon nanotubes are good candidates for gas storage because of their high specific surface area and large volume of pores. In Addition, it can be interesting to study the doping effects of Ag metal particles on specific surface of carbon nanotubes. Methane adsorption sites on pure multiwalled carbon nanotube (MWCNT) and Ag-doped MWCNT material system have been investigated using molecular dynamics (MD) simulations and density functional theory (DFT). The aim of this research study is to investigate the methane adsorption sites on pure and Ag-doped MWCNT and interactions between methane molecule and multiwalled carbon nanotube. In the current study, methane molecule has been simulated as adsorbate on pure and Ag-doped MWCNT to find the energy adsorption sites and to investigate the preferential adsorption of the methane molecule onto nanostructure. The study was made using Adsorption locator and DMol$^3$ module in Accelrys Materials Studio software. The methane adsorption energies for Ag-doped MWCNT are larger than that of the pure MWCNT. The interaction energy of a single methane molecule on multiwalled carbon nanotube, which follows the trend Eb (Ag-doped MWCNT) > Eb (MWCNT), where Eb denotes the binding energy of the methane molecule to the nanostructure. This result shows that Ag-doped MWCNT material system can be good methane storage medium.

**Keywords:** multiwalled carbon nanotube (MWCNT), Ag-doped MWCNT, methane storage

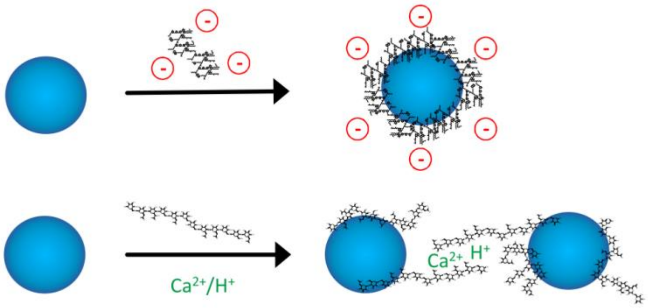
## P1-16

# Interactions of dissolved organic matter with inorganic colloids: a review

*Allan Philippe and Gabriele E. Schaumann*
Institute for Environmental Sciences, Department of Environmental and Soil Chemistry, University of Koblenz-Landau, Landau / Germany

E-mail: philippe@uni-landau.de

## Abstract



Understanding and quantifying the interactions of natural and artificial colloids with natural dissolved organic materials (DOM) is crucial to determine their behaviors under natural conditions. Humic substances, polysaccharides and proteins can adsorb onto the surface of most colloids and modify their physical and chemical properties. Magnitude and mechanism of adsorption depend on the particle, DOM type, and media composition. However, general tendencies can be seen for metal-oxide particles. The structure of adsorption layers can be highly complex and depends on all parameters cited above. If present, a coating agent can be replaced or overcoated by DOM.  In most systems, the adsorption layer completely modifies the colloidal stability of the sorbent. While humic substances tend to stabilize colloids upon agglomeration and deposition through electrostatic and steric effects, long polysaccharides or polypeptides tend to induce bridging-flocculation. The chemical properties of the colloid like dissolution are also influenced by DOM, although a clear mechanistic understanding of this influence is lacking. Despite important advances, many aspects concerning the adsorption of DOM onto metallic particles, its influence on hetero-agglomeration and the chemical reactivity of colloids require further investigations to be fully understood.

**Keywords:** dissolved organic matter, colloids, agglomeration, adsorption

## P1-17

# Sorption of engineered silver nanoparticles to environmental and model surfaces

*Priya Mary Abraham*[1], *Thomas Baumann*[2], *and Gabriele E. Schaumann*[1]
[1]Environmental and Soil Chemistry, University Koblenz-Landau, Landau / Germany
[2]Institute of Hydrochemistry, Technische Universität München, Munich / Germany

E-mail: schaumann@uni-landau.de

## Abstract

The fate of engineered nanoparticles in the environment is strongly determined not only by their tendency to form homo- or heteroaggregates but also by their interaction with environmental surfaces like plant leaves, soil particles, sediments or biofilms. In this study we are investigating the deposition behaviour of silver nanoparticles to model and environmental surfaces and to understand the role of particle-surface interaction forces for the quality and quantity of nanoparticle deposition.

Surface-nanoparticle interactions were investigated in batch experiments via equilibrium sorption isotherms to various natural and model surfaces. The model surfaces were chosen to cover a wide range of intermolecular interactions considering van-der Waals interactions as well as proton donor and acceptor interactions.

All the sorption isotherms for sorption of silver nanoparticles to different model surfaces were described best by Langmuir sorption. The Langmuir adsorption coefficient is controlled by the chemical nature of the model surfaces used.

The sorption study was accompanied by atomic force microscopy (AFM) on a qualitative and a quantitative basis for assessment of morphology and nanomechanical parameters of the covered surfaces.

In this contribution, we will discuss the physicochemical aspects of sorption and deposition of silver nanoparticles on environmental surfaces and the resulting environmental effects with special respect to quantitative aspects of sorption and interaction.

# Poster Session

# Toxicity

## Room: Refectory

**P2-01**

# Ecotoxicological screening test of surface coated silver nanoparticles on multiple luminescent bacteria

*Younjung Jung, Seungyun Baik, Jongwoon Kim, Hyunpyo Jeon, and Sanghun Kim*
Convergence Environment Team, KIST Europe, Korea Institute of Science and Technology, Saarbruecken / Germany

E-mail: yjjung@kist-europe.de, sbaik@kist-europe.de

## Abstract

Luminous microbial array for risk assessment (LumiMARA) using multi-strains of bacteria was applied for toxicological evaluation of 4 different surface coated AgNPs with average particle size of 20 nm. Coated materials for AgNPs were citrate (Cit), tannic acid (Tan), polyethylene glycol (PEG), and ranched polyethyleneimine (BPEI). In order to analyse the ecotoxicological mechanism, effects of physical characterization of target nanoparticles on the toxicity were compared by $EC_{50}$ achieved from dose-response curves. The tendency of toxicity effects for target AgNPs on 9 marine bacteria are following order; BPEI-AgNP (moderate salt stability, highly positive charge) > PEG-AgNP (high salt stability, moderately negative charge) > Tan-AgNP (moderate salt stability, highly negative charge) > Cit-AgNP (low salt stability, highly negative charge). Positively charged AgNPs with higher salt stability showed more toxic on luminescent bacteria. In addition of salt stability and surface charge, silver ions released from AgNPs were measured by titration method using iodide ($1.01 \times 10^{-4}$ mM) as a titrant by silver ion selective electrode (ISE). The concentration of silver ions released from BPEI-AgNP which showed more toxic than PEG-AgNPs was calculated as $1.16 \times 10^{-6}$ mM ($1.25 \times 10^{-4}$ mg/L), while silver ions released from PEG-AgNP could not be achieved. Consequently, salt stability, surface charge, and silver ions released are important factors caused the toxicity of surface coated AgNPs.

**Keywords:** surface coated AgNPs, luminescent bacteria, ecotoxicological screening test, surface charge of AgNPs

P2-02

# Integrating classical and molecular approaches to evaluate the impact of nanosized zero-valent iron (nZVI) on soil organisms

*Maria Ludovica Sacca*[2], *Carmen Fajardo*[1], *Gonzalo Costa*[1], *Carmen Lobo*[3], *Mar Nande*[1], *and Margarita Martin*[1]
1 Facultad de Veterinaria, Universidad Complutense de Madrid, Madrid / Spain
2 Moncloa Campus of International Excellence (UCM-UPM), Madrid / Spain
3 Instituto Madrileño de Investigación y Desarrollo Rural, Agrario y Alimentario (IMIDRA), Finca ‘‘El Encín’’, Madrid / Spain

E-mail: margamar@ucm.es, costag@ucm.es, cfajardo@ucm.es, mnande@ucm.es, carmen.lobo@madrid.org, ludovicasacca@ucm.es.

## Abstract

Nanosized zero-valent iron (nZVI) is a new option for the remediation of contaminated soil and groundwater, but the effect of nZVI on soil biota is mostly unknown. In this work, nanotoxicological studies were performed in vitro and in two different standard soils to assess the effect of nZVI on autochthonous soil organisms by integrating classical and molecular analysis. Standardised ecotoxicity testing methods using *Caenorhabditis elegans* were applied in vitro and in soil experiments and changes in microbial biodiversity and biomarker gene expression were used to assess the responses of the microbial community to nZVI. The classical tests conducted in soil ruled out a toxic impact of nZVI on the soil nematode *C. elegans* in the test soils.

The molecularanalysis applied to soil microorganisms, however, revealed significant changes in the expression of the proposed biomarkers of exposure. These changes were related not only to the nZVI treatment but also to the soil characteristics, highlighting the importance of considering the soil matrix on a case by case basis. Furthermore, due to the temporal shift between transcriptional responses and the development of the corresponding phenotype, the molecular approach could anticipate adverse effects on environmental biota.

**Keywords:** Nanosized zero-valent iron, Soil, Toxicity, Bacteria, *C. elegans*

**P2-03**

# Application of zero-valent iron nanoparticles (nZVI) to metal immobilization in an acidic soil: ecotoxicological impact

*M. Mar Gil-Díaz*[1], *Luis. T. Ortiz*[2], *Gonzalo Costa*[2], *Juan Alonso*[1], *M. Luisa Rodríguez-Membibre*[2], *Sebastian Sánchez-Fortún* [2], *Araceli Pérez-Sanz*[1], *Margarita Martín*[2], *and M. Carmen Lobo*[1]
[1]IMIDRA, Finca "El Encín", Alcalá de Henares, Madrid / Spain.
[2]Facultad de Veterinaria, Universidad Complutense de Madrid, Madrid / Spain

E-mail: mar.gil.diaz@madrid.org, ltortiz@vet.ucm.es, costag@vet.ucm.es, juan.alonso.canto@madrid.org, membibre@vet.ucm.es, fortun@vet.ucm.es, araceli.perez@madrid.org, margamar@vet.ucm.es, carmen.lobo@madrid.org

## Abstract

In recent years, the environmental application of nanoscale zero-valent iron (nZVI) has generated a great deal of attention due to its potential for cost reduction compared to other in situ treatments. The direct application of nZVI for soil remediation is a potential entry of nZVI into groundwater. Thus, characterizations of soil leachates as well as their potential toxicity have become crucial in evaluating the impact of ZVI nanoparticles in soil remediation. To date, little information exists on the assessment of nZVI-soil interactions. In this study a column experiment was conducted to evaluate the effectiveness of nanoscale zero-valent iron (nZVI) for the *in situ* immobilization of Pb and Zn in an acidic soil. The impact of nZVI on soil was evaluated by monitoring the physico-chemical characteristics of the leachates and their ecotoxicological effects on three species, *Vibrio fischeri*, *Artemia franciscana* and *Caenorhabditis elegans*. Treatment with nZVI resulted in more effective Pb immobilization in comparison to Zn and reduced the leachability by 98% and 72%, respectively; the immobilization was stable throughout the experiment. Leachates from ZVI-treated soils showed lower toxicity than leachates from untreated ones. The highest toxicity was observed in the first leachate, which presented high values of electric conductivity due to the leachability of soil ions, especially $Na^+$ from commercial nanoparticles. *V. fischeri* and *C. elegans* were more sensitive to leachates from nZVI-treated soils polluted with Zn than those from soils polluted with Pb; *A. franciscana* showed the opposite trend.

**Keywords:** nZVI, immobilization, Pb, Zn, column leaching, ecotoxicological effects.

**P2-04**

# Fate of CuO and ZnO nano- and micro-particles in the plant environment

*David W. Britt* [1], *Christian O. Dimkpa*[2], *Joan E. McLean*[3], *Drew Latta*[4], *Maxim I. Boyanov* [4], *and Anne J. Anderson*[2]

[1]Department of Biological Engineering, Utah State University, Utah / USA

[2]Department of Biology, Utah State University, Utah / USA

[3]Utah Water Research Laboratory, Utah State University, Utah / USA

[4]Biosciences Division, Argonne National Laboratory, Argonne, Illinois / USA

E-mail: david.britt@usu.edu, cdimkpa@usu.edu, joan.mclean@usu.edu, dlatta@anl.gov, mboyanov@anl.gov, anne.anderson@usu.edu

## Abstract

The environmental fate of metal oxide particles as a function of size was assessed by comparing the behavior of CuO or ZnO nanoparticles (NPs) to that of the corresponding microparticles (MPs) in a sand matrix, with and without wheat (*Triticum aestivum* L.) growth. After 14 days of incubation in the planted sand, the CuO and ZnO NPs increased from their nominal sizes of <50 nm and <100 nm, to ∼317 nm and ∼483 nm, respectively. Accordingly, the negative surface charge of colloids present in aqueous extracts from the sand amended with CuO (-27.0 mV) and ZnO (-10.0 mV) NPs was reduced by the presence of plants, to -19.8 mV and -6.0 mV, respectively. Plants did not influence the surface charge of the MPs. Plant growth increased dissolution of NPs and MPs of both metal oxides in the sand from <0.3 mg/kg to about 1.0 mg/kg for the CuO products, and from ≤0.6 mg/kg to between 1.0 and 2.2 mg/kg for the Zn products. The NP or MP products reduced wheat root length by ∼50-60% from control levels; CuO was more toxic than ZnO. X-ray absorption spectroscopy (XAS) analysis showed that treatments with MPs or NPs of ZnO led to similar accumulations of Zn−phosphate species in the shoots, likely from dissolution of ZnO. Exposure to CuO NPs or MPs resulted in similar XAS spectra for Cu in the shoots explained by plant accumulation of both CuO and CuI−sulfur complexes. These findings demonstrate the similarities between commercial NPs and MPs of CuO or ZnO in wheat plants, with greater root toxicity correlating with smaller particle size. Factors from the sand and the plant modified the aggregation or dissolution of both types of particles, thus, influencing their environmental fates.

**Keywords:** CuO, ZnO, wheat, *Triticum aestivum* L., ion uptake, growth inhibition

P2-05

# Acute and chronic toxicity of aged titanium dioxide nanoparticles on *Daphnia magna*

*Simon Lüderwald*[1], *Frank Seitz*[1], *Ricki R. Rosenfeldt*[1], *Ralf Schulz*[1], *and Mirco Bundschuh*[1,2]

[1]Institute for Environmental Sciences, University of Koblenz-Landau, Campus Landau / Germany

[2]Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Uppsala / Sweden

E-Mail: luederwald@uni-landau.de, seitz-f@uni-landau.de, rosenfeldt@uni-landau.de, schulz@uni-landau.de, mirco.bundschuh@slu.se

## Abstract

Due to the frequent application and potential release of titanium dioxide nanoparticles (n$TiO_2$) into surface waters, multiple studies have investigated their potential ecotoxicological implications on aquatic life. Thereby, toxicity tests with the standard test organism *Daphnia magna* revealed a high variability in the observed endpoints. In this context, particle characteristics are one important parameter while environmental conditions (e.g. organic matter (OM)) may represent further explanatory variables. However, the aging of nanoparticles under different environmental conditions is rarely considered. Therefore, the present study investigated acute and chronic effects of differently aged n$TiO_2$ (A100, ~100 nm) on *D. magna*. In a first step 96-h acute toxicity tests with n$TiO_2$, aged (0, 1, 3, 6-d) in presence and absence of dissolved organic matter (±DOM) in media with varying ionic strength (MilliQ water or ASTM-medium), were conducted. In addition, 21-d chronic experiments with 0 and 3-d aged n$TiO_2$ (ASTM-medium (±DOM)) were carried out. The acute toxicity test with n$TiO_2$ aged in MilliQ water (±DOM) did not reveal any significant differences among the observed 96-h $EC_{50}$ (0.56-1.41 mg/L). In contrast, a 6-d aging of n$TiO_2$ in ASTM-medium in absence of DOM caused a fourfold decrease in toxicity, compared to the 0-d aging. However, for ASTM-medium in presence of DOM the n$TiO_2$ toxicity increased by ~50% after the 3-d aging, while 6-d of aging decreased the toxicity by ~60% relative to 0-d aging. Chronic experiments showed effects of unaged n$TiO_2$ on the survival of *Daphnia* at 2.00 mg/L (-DOM). In contrast 3-d aged n$TiO_2$ in ASTM-medium caused a reduced toxicity indicated by a decreased mortality but an inhibition of reproduction of ~60% at 2.00 mg/L (-DOM) and ~50% at 6.00 mg/L (+DOM). The present study suggests that aging of n$TiO_2$ in presence of DOM modifies the toxicity in a condition-specific manner. Therefore it seems reasonable considering the aging process during future investigations as well as environmental risk assessment.

**Keywords:** nanoparticles, aging, dissolved organic carbon, reproduction, crustacea

**P2-06**

# Implications of low titanium dioxide nanoparticle concentrations on the ecotoxicological potential of copper for *Daphnia magna*

Theresa Schell[1], Ricki R. Rosenfeldt[1], Frank Seitz[1], Ralf Schulz[1], and Mirco Bundschuh[1,2]
[1]University of Koblenz-Landau, Campus Landau, Institute for Environmental Sciences, Landau / Germany
[2]Swedish University of Agricultural Sciences, Department of Aquatic Sciences and Assessment, Uppsala / Sweden

E-mail: sche3624@uni-landau.de, rosenfeldt@uni-landau.de, seitz-f@uni-landau.de, schulz@uni-landau.de, mirco.bundschuh@slu.se

## Abstract

The increasing use and production of titanium dioxide nanoparticles ($nTiO_2$) raises concerns regarding their unintentional release into the aquatic environment. There, $nTiO_2$ may co-occur with other chemical stressors, such as heavy metals, potentially altering the bioavailability of these substances: metals may adsorb to $nTiO_2$ followed by agglomeration and sedimentation (reduced toxicity). However, particles with high amounts of adsorbed copper could also be ingested by organisms ultimately causing an increased body burden (increased toxicity). In the present study implications of various $nTiO_2$ (P25, ~100 nm) concentrations on the copper toxicity were investigated employing 72-h acute toxicity tests with *Daphnia magna*. The experiments uncovered a statistically significant increased copper toxicity (9%) in the presence of 50 µg $nTiO_2$/L relative to their absence. In contrast, the highest $nTiO_2$ concentration tested (2000 µg/L) did not statistically significantly influence the copper toxicity. The small increase in toxicity could not be reliably reproduced in the course of subsequent experiments. Therefore further investigations were carried out to assess for potential influences of daphnids' age on the test outcome using two different age classes (0-6 and 18-24 h). Due to the theoretically possible variation of *Daphnia´s* age up to 24 h at the test start, the two age classes with the maximum possible age difference were chosen. Indeed, the younger age class (0-6 h) displayed a statistically significant increased copper toxicity (34%) in presence of 50 µg $nTiO_2$/L relative to copper alone, while for older organisms (18-24 h) the copper toxicity was not affected at this $nTiO_2$ concentration. These results indicate depending on the $nTiO_2$ concentration different implications on other chemical stressors. Moreover, even low concentrations could severely increase the toxicity of these stressors. These results highlight the need for further studies in this context to uncover the underlying mechanisms.

**Keywords**: $nTiO_2$, heavy metals, crustacea, age-dependence

# Poster Session

# Analytics

Room: Refectory

**P3-01**

# OECD protocols for a tiered determination of nanomaterial dispersions behaviour in different environmental media

*Frank von der Kammer* [1], *Andreas Gondikas*[1], *Boris Meisterjahn*[1], *Kathrin Schwirn*[2], *Doris Voelker*[2], *and Thilo Hofmann*[1]

[1]Environmental Geosciences Group, University of Vienna, Vienna / AU

[2]Federal Environmental Agency, Dessau-Rosslau / Germany

E-mail: frank.von.der.kammer@univie.ac.at, andreas.gondikas@univie.ac.at, boris.meisterjahn@univie.ac.at, Kathrin.Schwirn@uba.de, Doris.Voelker@uba.de, thilo.hofmann@univie.ac.at

## Abstract

Whether a substance or a material is regarded as “nano” depends on the definition and classification scheme used. Those definitions might differ across sectors (environment, food, cosmetics, electronics, etc.). ISO defines nanomaterials as: “a material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale (1 – 100 nm)”. In comparison, the EU Commission recommendation on the definition of nanomaterials is (2011/696/EU): ‘nanomaterial’ means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 – 100 nm. However, one pressing issue is the specific testing of nanomaterials along the OECD guidelines. The incorporation of ‘aggregation state’ and ‘number size distribution’ in the recommendation indicates that test protocols, like OECD test guidelines, that have originally been developed for traditional chemical compounds might require adjustments to account for nanomaterial-specific properties and processes. The resistance of a material against dispersion in aqueous media on one hand and the tendency and degree of the material to agglomerate on the other hand need to be taken into account for developing test protocols and designing test strategies since these properties, beside e.g. the materials solubility, considerably influences the further fate and behaviour of nanomaterials in the environment and in the test systems. This project aims at i) developing a decision tree for the determination of nanomaterials’ dispersion and dispersion behaviour and ii) developing specific experimental procedures for testing the dispersibility and dispersion behaviour of nanomaterials in different environmental media. This development is undertaken within the framework of OECD Test Guideline Program on initiative of the OECD WPMN. This guidance will be based upon a conceptual framework, experimental protocols, such as powder dispersion in liquid media using sonication, and time-resolved particle size and concentration measurements under different environmentally relevant conditions. The development of these protocols is the first imperative step of the new development and the nanomaterials specific amendment of existing OECD test guidelines and guidance documents. It will deliver important information on nanomaterials that is necessary to determine and assess the fate and behaviour of nanomaterials in the environment.

**Keywords:** definition, nanomaterial, protocol, dispersibility, dispersion stability, OECD Test Guidelines

**P3-02**

# Speciation of phosphorus and colloidal Fe and Al (hydr)oxide complexes in different particle size fractions of an arable soil

*Xiaoqian Jiang*[1] , *Roland Bol*[1], *Sabine Willbold*[2], *and Erwin Klumpp*[1]
[1]Institue of Bio- and Geosciences, Agrosphere (IBG-3)
[2]Central Institute for Engineering, Electronics and Analytics, Analytics (ZEA-3)
Research Center Jülich, Jülich/ Germany

E-mail: x.jiang@fz-julich.de, r.bol@ fz-juelich.de, s.wilbold@fz-juelich.de, e.klumpp@fz-juelich.de

## Abstract

Soil organic and inorganic phosphorus are in the majority of cases stabilized through the association with mineral components, especially with Fe and Al (hydr)oxides. However, few studies have focused on the relative contributions of different organic and inorganic forms of P bound to Fe and Al oxide colloids. In our arable soil study, amorphous and crystalline minerals were separated by selective dissolution with oxalate acid and dithionite–citrate from various particle-size fractions (>2000, 450-2000, 100-450, and 1-100 nm). Asymmetric flow field-flow fractionation (AF4) coupled to inductively coupled plasma mass spectrometer (ICP-MS), solution $^{31}$P-nuclear magnetic resonance spectroscopy (NMR) and transmission electron microscopy (TEM) were employed. They were used to examine the speciation and contribution of (inorganic and organic) P bound to amorphous and crystalline Fe and Al (hydr)oxides in several soil fractions and to study the mechanism behind P fixation to these colloids in arable soil.

Results showed that colloids and nanoparticles have higher amounts of Fe, Al and P than larger sized particles. P is, to a large extent, associated with amorphous Fe and Al (hydr)oxides. Soil nanoparticles <100nm revealed two size fractions measured by AF4. The smaller size fractions (below 5nm) consist of natural organic matter (NOM) with a high UV-absorbance and P content. The larger size fraction (approximately 60nm) is a complex of Fe and Al (hydr)oxides linked to P, clays and NOM. Furthermore, it is more likely that the P absorbed to NOM is bound to crystalline rather than to amorphous Fe and Al (hydr)oxides.

**Keywords:** phosphorus; colloidal and nanoparticulate Fe and Al (hydr)oxides; NOM;

**P3-03**

# Separation and quantification of nanoparticles in aqueous samples using cloud-point extraction

*Georg Hartmann and Michael Schuster*
Technische Universität München, Department Chemistry, München / Germany

E-mail: georg.hartmann@tum.de, michael.schuster@tum.de

## Abstract

For the quantification of metal nanoparticles (NPs) in aqueous samples several possible methods have been proposed, with each of them showing distinct advantages but also major drawbacks. Especially matrix tolerance is a crucial issue if samples like wastewater treatment plants (WWTPs) are to be analyzed. It is a major challenge for any analytical technique to cope with such samples.

Cloud-point extraction (CPE) is a very facile technique that has been shown to selectively extract NPs in the presence of ions of the same element. In combination with ET-AAS, CPE allows for the selective determination of NPs of a given element even in complex samples with detection limits in the low ng per L level [1, 2]. Extraction parameters, however, have to be optimized for any type of NPs individually. For silver NPs (Ag-NPs) we show a thorough validation of the method in terms of matrix tolerance, but also with respect to NP surface-coatings. We found little or no influence of the simulated matrices tested and no influence for > 90 % of all surface coatings tested [3].

The fact that virtually any NPs are extracted, even in complex systems, together with the method's simplicity and accessibility make it an ideal tool for the determination of a sum parameter, e.g. total nanosized silver in water samples [4]. Besides this, CPE was also be used to address other NP-related problems like stability or formation of NPs.

## References

[1] Georg Hartmann, Christine Hutterer, Michael Schuster; *Journal of Analytical Atomic Spectrometry*, **28** (2013) 567 - 572.
[2] Georg Hartmann, Michael Schuster; *Analytica Chimica Acta*, **761** (2013) 27 - 33.
[3] Georg Hartmann, Tanja Baumgartner, Michael Schuster; *Analytical Chemistry*, **86** (2014) 790-796.
[4] Lingxiangyu Li, Georg Hartmann, Markus Döblinger, Michael Schuster; *Environmental Science & Technology*, **47** (2013) 7317 - 7323.

**Keywords:** metal nanoparticles, quantification, water, wastewater, cloud point extraction

**P3-04**

## 3D Distribution of retained silver particles in unsaturated porous media

*Veronica L. Morales* [1], *Francisco J. Perez-Reche*[2], *Markus Holzner*[3], *Wolfgang Kinzelbach* [3], *and Wilfred Otten*[1]

[1]SIMBIOS Center, University of Abertay, Dundee / UK

[2]Institute for Complex Systems and Mathematical Biology, University of Aberdeen, Aberdeen / UK

[3]Institute for Environmental Engineering, ETH Zurich, Zurich / CH

E-mail: v.morales@abertay.ac.uk

### Abstract

It is well accepted that colloid and nanoparticle transport processes in porous media differ substantially between water saturated and unsaturated conditions. Differences are frequently ascribed to particle immobilization by association with interfaces with the gas, as well as to restrictions of the liquid medium through which colloids are transported. Such factors depend on interfacial conditions provided by the water saturation of the porous medium. Yet, the current understanding of the importance of particle retention at gas interfaces is based on observations of single pores or two-dimensional pore network representations, leaving open the question of their statistical significance when all pores in the medium are considered. In order to address this question, column experiments were performed using a model porous medium of glass beads through which Silver particles were transported for conditions of varying water content. X-ray microtomography was subsequently employed as a non-destructive imaging technique to obtain pore-scale information of the entire column regarding: i) the presence and distribution of the four main locations where colloids can become retained (interfaces with the liquid-solid, gas-liquid and gas-solid, and the bulk liquid), ii) deposition profiles of colloids along the column classified by the available retention location, iii) morphological characteristics of the deposited colloidal aggregates, and iv) channel widths of 3-dimensional pore-water network representations. The results presented provide, for the first time, a direct statistical evaluation on the significance of colloid retention by attachment to the liquid-solid, gas-liquid, gas-solid interfaces, and by straining in the bulk liquid. Additionally, an effective-pore structure characteristic is proposed to improve predictions of mass removal by straining under various water saturations.

P3-05

# Effects of surfactants and buffers on stability and electrophoretic mobility of gold nanoparticles

*Denis Rakcheev, George Metreveli, and Gabriele E. Schaumann*
Institute of Environmental Sciences, Department of Environmental and Soil Chemistry, University of Koblenz-Landau, Landau / Germany

E-mail: rakcheev@uni-landau.de

## Abstract

Gel electrophoresis in combination with inductively coupled plasma mass spectrometry (GE-ICP-MS) is commonly used for the characterisation of metal-caped DNA molecules and metalloproteins. Usage of this method for the characterisation of submicron particles is, however, limited due to the difficulty in migration of particles through gel phase. A number of recent works investigating the application of the GE-ICP-MS for the analysis and separation of nanoparticles reported a distinct peak tailing. Due to electrophoretic migration through the sieving media and agglomeration of particles which can be induced by electrophoretic forces or chemical composition of the medium, the signal intensity in chromatograms represented by a very broad peak of corresponding elements. In this work we attempt to optimize media and conditions for narrowing the distribution of gold nanoparticles along the gel. We will discuss how different electrolytes (used as buffer solutions) and surfactants (used as particle stabilizers) of various concentrations affect the size of the nanoparticles in the system and enhance their separation. These results are expected to be useful for the further development of GE-ICP-MS and also for highlighting the potentials of gel electrophoresis for possible hyphenation with a novel method of single particle ICP-MS.

**Keywords:** gel electrophoresis, gold nanoparticles, agglomeration

**P3-06**

# Effect of silver nanoparticles on surface properties of bacterial biofilm - An AFM study

*Sandra Barnikol*[1], *Alexandra Grün*[2], *Priya Mary Abraham*[1], *Dörte Diehl*[1], *Werner Manz*[2], *and Gabriele E. Schaumann*[1]

[1]University Koblenz-Landau, Institute of Environmental Sciences, Dept. Environmental and Soil Chemistry
[2]University Koblenz-Landau, Institute of Integrated Natural Sciences, Department of Biology

E-Mail: barnikol@uni-landau.de

## Abstract

Biofilms play an important role for self purification processes in aquatic environments and biological sewage treatment plants. Engineered silver nanoparticles have been used in different commercial products like medicine, textiles, and food industry. The amount of silver nanoparticles (*n*Ag) in consumer's products has successively increased, during the last years and hence the probability of silver release into environmental systems via waste water or sewage sludge is also increased. Thus, exposure of biofilms with *n*Ag is inevitable. However, effects of *n*Ag on the biofilm surface and its properties are up to now largely unknown. In this study, we investigated the effect of silver nanoparticles on a monospecies biofilm (*A. citratiphilum*) surface. *Peak force quantitative nano-mechanical mapping* (PF-QNM) mode of atomic force microscopy was used to measure the adhesion force between AFM tip and biofilm surface and elastic or plastic properties (dissipation) on the dried biofilm surface. Toxicity results show that *n*Ag treatment in a concentration of 600 µg $L^{-1}$ with 30 and 100 nm particle sizes are not cytotoxic to planktonic cells of *Aquabacterium citratiphilum*. However, it shows an influence on the adhesion force and dissipation characteristics of *Aquabacterium citratiphilum* biofilm. After 8 hrs treatment the adhesion forces towards *n*Ag treated biofilms were slightly reduced compared to untreated biofilm. However, with continuing treatment up to 24 hrs the adhesion force towards the treated biofilms increased again indicating that the force between AFM tip and biofilm surface became stronger. In accordance, during the first 8 hrs of treatment the dissipation value of the biofilm surface reduced slightly but after 24 hr its magnitude showed a sharp increase. From these results we can conclude that longer exposure of biofilms to *n*Ag may increase its plasticity.